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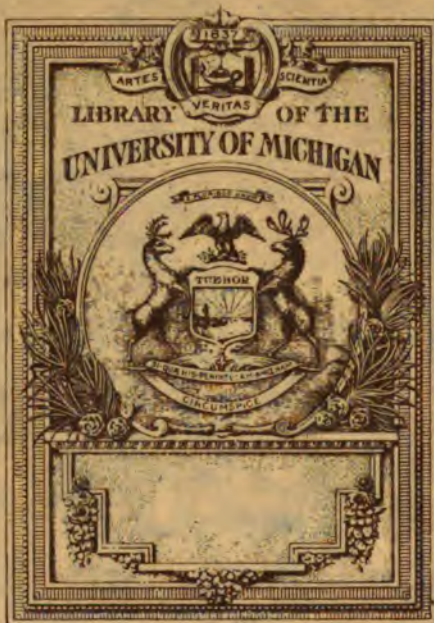
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LABORATORY

MANUAL OF CHEMISTRY,

MEDICAL AND PHARMACEUTICAL,

CONTAINING

EXPERIMENTS AND PRACTICAL LESSONS IN INORGANIC SYNTHETICAL WORK;
FORMULÆ FOR OVER THREE HUNDRED PREPARATIONS, WITH EXPLANATORY NOTES; EXAMPLES IN QUANTITATIVE DETERMINATIONS AND THE VALUATION OF DRUGS; AND SHORT SYSTEMATIC COURSES IN QUALITATIVE ANALYSIS AND IN THE EXAMINATION OF URINE.

BY

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WITH ORIGINAL ILLUSTRATIONS.

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PREFACE.

Our object in preparing this manual was to provide in convenient form a sufficient number of suitable lessons in laboratory work, and at the same time to embody in the book the facts of inorganic chemistry most important to pharmacy and medicine. It contains experiments intended to familiarize the student with the properties of the principal elements, lessons in synthetical chemistry, a systematic course in qualitative analysis, examples in quantitative determinations, including the official methods of assay for a few important drugs, and a short chapter on the chemical and microscopical examination of urine.

Among the lessons in Part II will be found the working formulæ of the pharmacopœias for many of the preparations.

Students pursuing synthetical work without an instructor can successfully and with benefit make most of the pharmaceutical preparations included in the Second Part, with the aid of the explanatory notes it contains. For purposes of practice the quantities of materials operated upon may, of course, be small and the outfit of apparatus limited to the list given in the appendix. The proportions of the materials are stated, sometimes in parts by weight, and sometimes in definite quantities expressed in terms of the metric system, which will afford useful practice in the application of both forms.

The portions devoted to analytical methods are necessarily much condensed, but believed to contain all that is essential in a work of this character.

THE AUTHORS.

CHICAGO, May, 1887.

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PART I.

ELEMENTS AND THEIR COMPOUNDS.

With Experiments.

THE NON-METALS.

CHAPTER I.

OXYGEN.

OXYGENIUM.

O. 15.96.

Sp. gr. ($\pi=1$) 15.96.

Oxygen is the most abundant of the elements, constituting 88.87 per cent. of water and 22.99 per cent of air.

The mass of the earth's crust is made up of old crystalline rocks containing about 45 per cent. of oxygen, in the mean.

The gas can be taken from the air by several indirect processes, but for most purposes it is obtained by the decomposition of some of its compounds.

Some of these decompositions are illustrated in the following experiments:

Exp. 1. Heat a few Gm. of mercuric oxide, HgO , in a tube of hard glass, held in the flame of a Bunsen burner. The red mass turns dark, and soon small globules of mercury can be seen on the cooler parts of the tube above the flame. At this stage hold a glowing

splinter just within the mouth of the tube. It will rekindle and burn brilliantly. This indicates the presence of oxygen liberated according to the following equation:

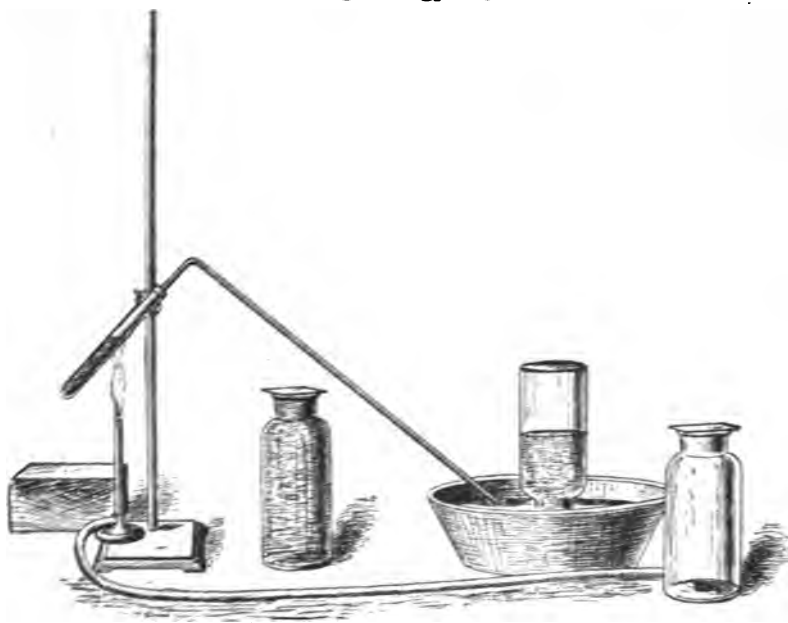
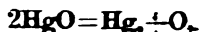
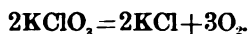


FIG. 1.

Exp. 2. Mix about 15 Gm. of powdered potassium chlorate, KClO_3 , with 5 Gm. of manganese dioxide, MnO_2 , and heat in a tube of hard glass connected with a delivery tube as shown in Fig. 1. The KClO_3 parts with the whole of its oxygen, as this equation indicates:



The manganese dioxide is not changed, but by its presence causes the chlorate to break up at a lower temperature than would be the case without it.

As soon as the air has been driven out of the tube, collect the escaping gas in wide-mouth bottles of 200 C.c. capacity. These bottles are first filled with water, covered with glass plates, and inverted so as to stand on a little bridge over the open end of a delivery tube. As each bottle fills, close it with a stopper or glass plate, and set aside for subsequent tests.

As the KClO_3 contains 39.1 per cent. of oxygen, the 15 Gm. should furnish about 400 C.c. of the gas.

This method is the one usually employed in making large quantities of oxygen for experiment, or for production of the calcium light.

Copper retorts, Fig. 2, holding from half a liter to four or five liters, are employed in such cases instead of glass, and the gas is collected in rubber bags, or in gasometers of zinc, copper, or plate iron. Five hundred Gm. of KClO_3 , mixed with 150 Gm. of MnO_2 , furnish about 120 liters of oxygen. Care should be taken to use dry materials, which must be free from organic matter. The MnO_2 is sometimes

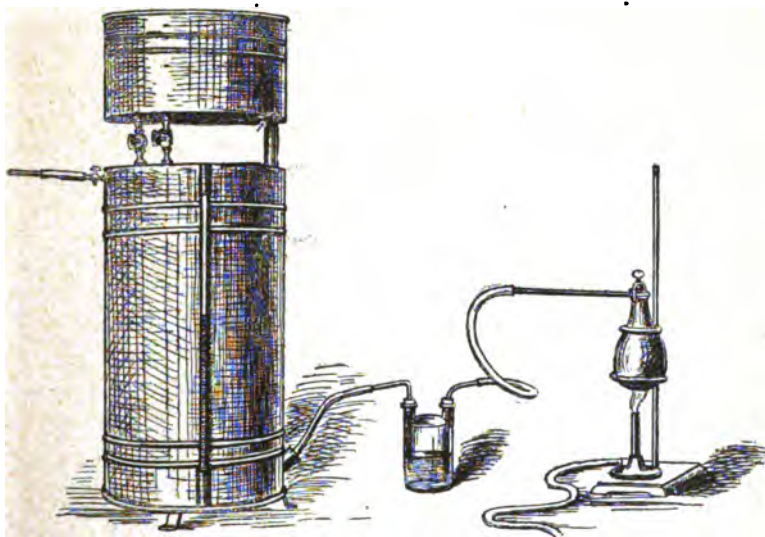
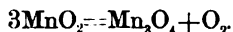


FIG. 2.

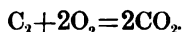
adulterated or accidentally mixed with carbonaceous matter (as powdered coal), and serious results have followed from the action of this on the liberated oxygen.

Manganese dioxide alone is sometimes used in making oxygen. It decomposes at a high temperature in this way:



The most striking property of oxygen is shown by its combination with various substances.

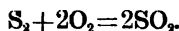
Exp. 3. Attach a piece of charcoal to a bent wire, bring it to a glowing condition in the lamp flame, and plunge it quickly in a bottle of the gas. It burns brilliantly, throwing off showers of sparks. Pour some lime-water in the bottle at the end of the reaction, close with a glass plate, and shake. A white precipitate is formed, owing to the combination of a constituent of the lime-water (calcium hydrate) with the gas produced by the combustion of the charcoal. The gas is carbon dioxide.



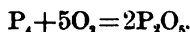
The precipitate consists of calcium carbonate.

Exp. 4. Melt a little sulphur in a deflagrating spoon, heat it until it begins to burn, and then plunge it into a bottle of oxygen. It will burn with a blue flame much brighter than in the air.

In this case sulphur dioxide is formed which can be recognized by its characteristic odor.



Exp. 5. Carefully dry a *very small* piece of phosphorus between folds of filter-paper, place it in a deflagrating spoon, ignite it by holding for a second in the lamp, and thrust quickly into a bottle of oxygen. Immediate combustion takes place, an intense white light is produced, and the bottle soon fills with fumes of phosphoric oxide, P_2O_5 .



In each of these three experiments an *oxide* was formed. By pouring water into the bottles and then testing this with litmus paper, it will be observed that in each case a body of acid reaction has been formed, as will be explained later.

A metal burned in the gas would be converted into a metallic oxide with properties very different from those of the compounds resulting from the above experiments.

Oxygen is sometimes used for inhalations. For this purpose it must be carefully washed by passing through two wash-bottles before reaching the gasometer.

The first bottle should contain solution of sodium or potassium hydrate.

OZONE.

The preparation of ozone, a form of oxygen, will be referred to when discussing some of the properties of iodine.

HYDROGEN.

HYDROGENIUM.

H. 1.

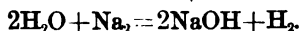
Sp. gr. ($n=1$) 1.

Hydrogen has been found free in nature in very small quantities, as in volcanic gases and emanations from oil wells.

Combined, it occurs abundantly, as in water and in animal and vegetable tissues.

It can readily be liberated by decomposing water by the electric current, or by the action of potassium or sodium.

Exp. 6. Enclose a piece of sodium in a small cylinder made of wire gauze to which is attached a wire handle. Fill a bottle with water and invert it in a pan of water by aid of a glass plate. Incline it a little to one side and quickly depress the cage with the sodium beneath its mouth. Bubbles of gas ascend and displace the water in the bottle, the decomposition taking place according to this equation:



For the success of this experiment the bottle must be quite filled with water, and the piece of sodium taken, small.

Hydrogen is commonly obtained by the action of zinc or iron on dilute sulphuric or hydrochloric acid.

Exp. 7. Some pieces of granulated zinc are placed in a bottle of 250 C.c. capacity fitted with a funnel tube and delivery tube as shown in Fig. 3, and covered with water. Dilute sulphuric acid, H_2SO_4 , is poured through the funnel tube, and immediately gives rise to the liberation of gas. This displaces the air, and in turn escapes from

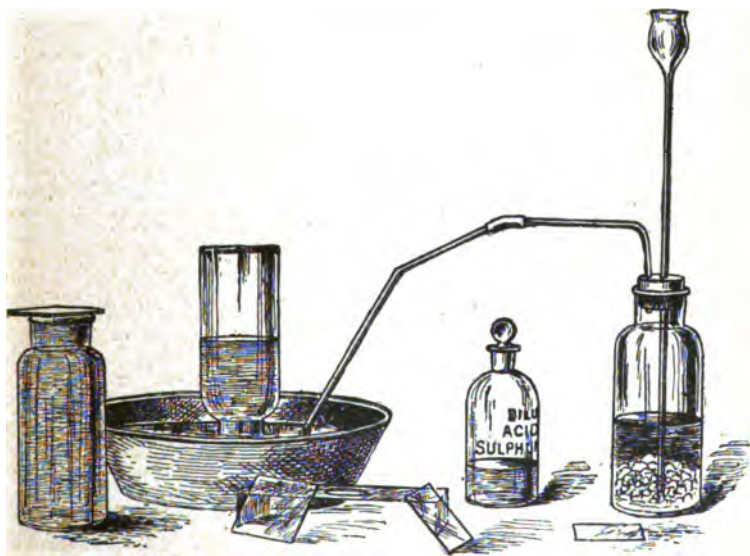
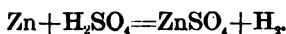


FIG. 3.

the delivery tube. The open end of the latter is placed under collecting bottles filled with water, as used in obtaining oxygen, and as fast as the bottles fill with the gas they are removed, still inverted, and kept for the tests to be described.

In this experiment care must be taken to allow the air to be completely expelled by the generated gas before saving it for experiment. Before the expulsion of the air it would not be safe to bring a light near the end of the delivery tube, as an explosion might follow from the ignition of the mixture of hydrogen and oxygen within the bottle.

The decomposition takes place in this way:



100 Gm. of zinc and 85 C.c. of strong sulphuric acid, diluted with 10 volumes of water, will furnish 34 liters of the gas.

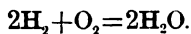
The gas can be tested in several ways.

Exp. 8. Thrust a lighted match or taper into a bottle held with its mouth downward. The gas burns with a clear flame while the flame on the end of the match within the bottle is extinguished.

Exp. 9. Make a mixture of hydrogen and air, by bringing an empty bottle, *mouth upward*, beneath one of the same size filled with gas held with its mouth downward. By keeping the bottles together and turning them so as to bring the upper one below, the two gases become mixed. By bringing them now to a flame a sharp explosion follows, from the union of the oxygen of the air and the hydrogen.

In the 8th experiment the light hydrogen in the inverted bottle excluded the air, which could only enter after the combustion.

Exp. 10. Remove the delivery tube from the still active generating bottle and attach a tube, drawn to a point, and directed upward; light the escaping gas, and hold a dry bottle over the flame. The inner walls soon become covered with a film of moisture from the water produced by the combustion of the hydrogen.



This experiment is conclusive in showing the formation of water only when the gas is dried by passing through a tube containing calcium chloride in small pieces, or pumice-stone moistened with strong sul-

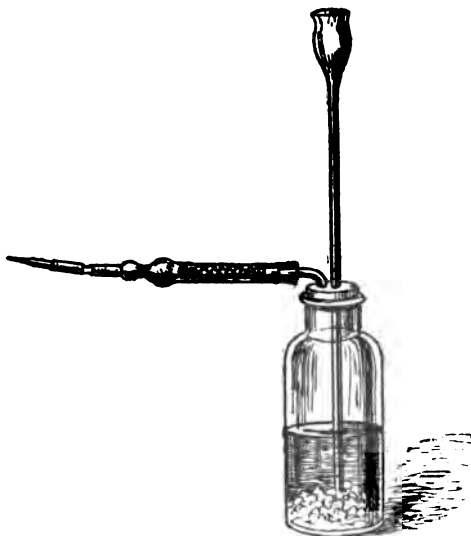
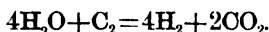
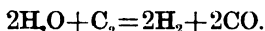


FIG. 4.

phuric acid. Either of those substances would remove the moisture mechanically carried along from the generator. (See Fig. 4.)

There are several processes by which more or less impure hydrogen can be made on a large scale, for filling balloons or for burning with oxygen, in producing a flame of great heat.

When steam is passed over charcoal or hard coal contained in a fire-clay retort and heated to whiteness, it is decomposed, the hydrogen being liberated, while the oxygen combines to form oxides of carbon, according to the following equations:



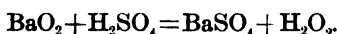
By properly regulating the heat and amount of steam passed, the decomposition may be made to take place chiefly according to the second equation, in which case the CO_2 formed can be absorbed by passing the gas over slaked lime, leaving nearly pure hydrogen.

HYDROGEN AND OXYGEN.

These gases unite to form water, as shown above. They also form a second compound, hydrogen dioxide or peroxide, H_2O_2 , of considerable practical importance.

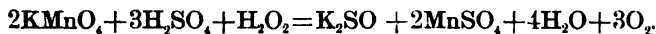
The chief properties and tests of water will be given in a subsequent chapter.

Hydrogen dioxide is a liquid of 1.452 specific gravity; but as in the pure condition it is very unstable, it is usually handled in water solution. It is best made by the action of barium dioxide on a dilute acid, as sulphuric:



Exp. 11. Add to 10 C.c. of dilute sulphuric acid (1 to 6) four or five Gm. of barium dioxide, a little at a time. When the white precipitate of barium sulphate has subsided filter the liquid and test it. It is a dilute solution of H_2O_2 . Immerse in a portion of it a strip of *ozone test paper*, prepared as described later. It will turn blue, proving a strong oxidizing action.

Add to the rest of it, acidified with dilute sulphuric acid, a solution of potassium permanganate. The color of the latter disappears. On this reaction is based a method of finding the amount of the H_2O_2 present in a solution.



CHAPTER II.

CHLORINE.

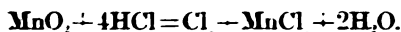
CHLORUM.

Cl 35.4.

Sp. gr. (=1) 35.4.

Chlorine does not occur free, but in combination, chiefly as sodium and potassium chlorides.

It is best prepared from one of its artificial compounds, hydrochloric acid, by heating this with something which has a strong affinity for the hydrogen of the acid. Manganese dioxide is commonly employed for this purpose, and the reaction which takes place is this:



Potassium bichromate is a second substance which may be used, with the reaction:

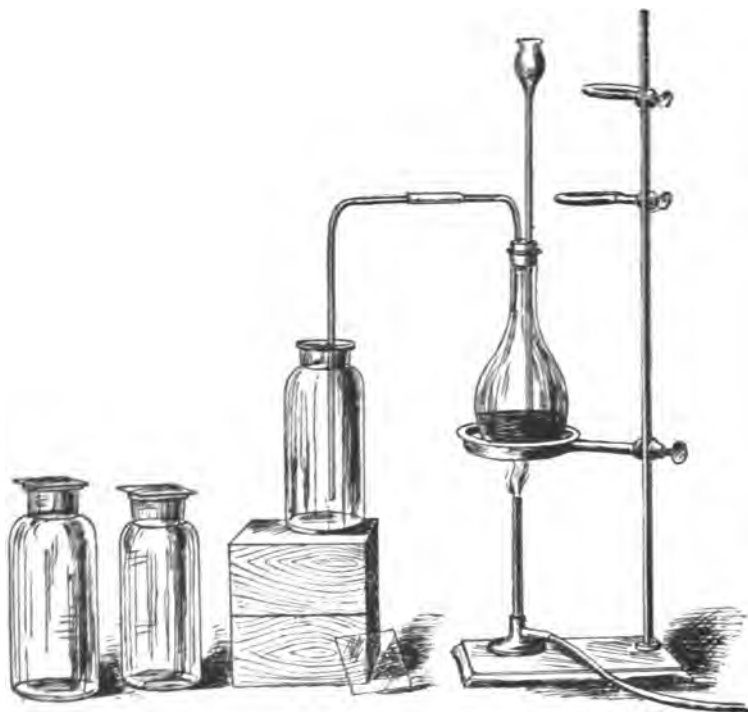
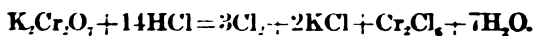


FIG. 5.

Exp. 12. Arrange a flask as shown in Fig. 5, and charge it with about 20 Gm. of the MnO_2 in small lumps or coarse powder, and about 50 C.c. of strong hydrochloric acid. Apply heat and collect the gas evolved by downward displacement, as represented in the figure, cover the bottles, as filled, with glass plates, and apply the tests given below.

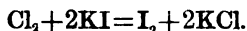
It will be noticed that the greenish yellow gas possesses a disagreeable pungent odor. Care must be taken not to inhale much of it, as it is extremely irritating to the air passages. Experiment has shown that it is about two and one-half times as heavy as air. It has a very great affinity for many of the metals, combining with some of them to produce light and heat. It combines readily with hydrogen, and in some cases can displace other elements to enter into such combination. It can likewise displace bromine and iodine to combine with metals.

Exp. 13. Remove the cover from one of the bottles, and by means of a piece of gauze sift in some powdered antimony. Vivid combustion takes place, and white fumes of chloride of antimony fill the bottle.

Exp. 14. Warm a little oil of turpentine in a test tube, and immerse in it a strip of filter-paper. Dip this now in a second bottle of the gas, and notice that it soon commences to smoke and finally bursts into flame. The oil of turpentine consists of carbon and hydrogen, the former of which is liberated as soot, when the hydrogen combines with the chlorine to form HCl .

Exp. 15. Moisten a bit of printed cotton goods (calico) in water and hang it in a bottle of the gas; after a time it becomes bleached. The coloring matter contains substances easily acted upon by chlorine itself, or by the *oxygen* liberated from water by the action of the chlorine. The perfectly dry gas bleaches only after prolonged action, in which case the whole fabric may be destroyed.

Exp. 16. Make a paste by boiling some starch with water containing a little potassium iodide; spread this on strips of paper, which immerse in a bottle of the gas. A blue color appears immediately on the paper, due to the action of the liberated *iodine* on starch, as soon to be explained. The chlorine in this experiment displaces iodine to combine with potassium.



Chlorine is used on a large scale for bleaching, and for this purpose it is liberated from "bleaching powder" by some acid. Bleaching powder contains, as its active ingredient, calcium hypochlorite, which is readily decomposed by acids, even by the carbonic acid of the air, with liberation of chlorine.

Exp. 17. Place some bleaching powder in a beaker and pour over it a little acid, as moderately dilute H_2SO_4 . The gas is liberated, and soon fills the bottle. The tests given above can be applied.

For bleaching on the large scale it is simply necessary to moisten the goods and hang them in rooms, the floors of which are covered by a layer of the powder. The carbonic acid in the air gradually liberates chlorine, which in turn acts on the coloring matter present in the raw goods.

A more rapid process is to dip the goods in a dilute acid and then in a solution of the powder, repeating the operation several times, and washing finally with water.

CHLORINE FUMIGATION.

A room can be fumigated, after removal of furniture, clothing or other articles liable to be spoiled, by placing in a shallow plate or dish 20 Gm. of powdered MnO_2 and 50 C.c. of strong HCl , closing the doors and windows and leaving this in the center of the room on a box or table.

If these materials are not at hand, "bleaching powder" and vinegar may be substituted, but a large excess of vinegar would be required, and the action would be slow.

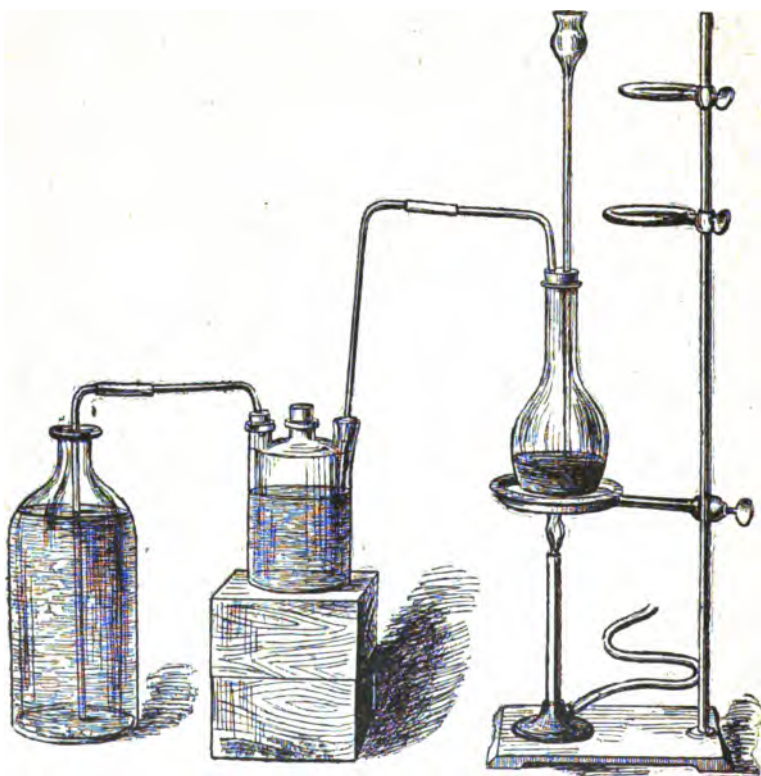


FIG. 6.

CHLORINE WATER.

AQUA CHLORI.

Chlorine water is a solution of the gas in water, and can be prepared by conducting it from the generating flask into a bottle or beaker of water.

For pharmaceutical uses it is necessary to wash the gas by passing it through the water of a single Woulfe bottle (as shown in Fig. 6) before leading it into the distilled water to be saturated. The proportions in Exp. 12 are sufficient for making a liter of chlorine water: heat

should not be applied to the generating flask at first, and finally only gently. The wash-bottle is used to retain small amounts of hydrochloric acid which are carried along with the chlorine. The receiving bottles of about 250 C.c. each should be kept at a temperature of about 10°C ., and when the water in them is saturated, they should be tightly stoppered (with glass) and kept in a dark cool place. The point of saturation can be learned by stopping a bottle and shaking it thoroughly. If the greenish yellow gas is still seen above the water enough has been passed in. Otherwise, it should be further charged. The solution should contain 0.4 per cent. of chlorine, and its value can be found by applying the appropriate test given under the head of Volumetric Analysis.

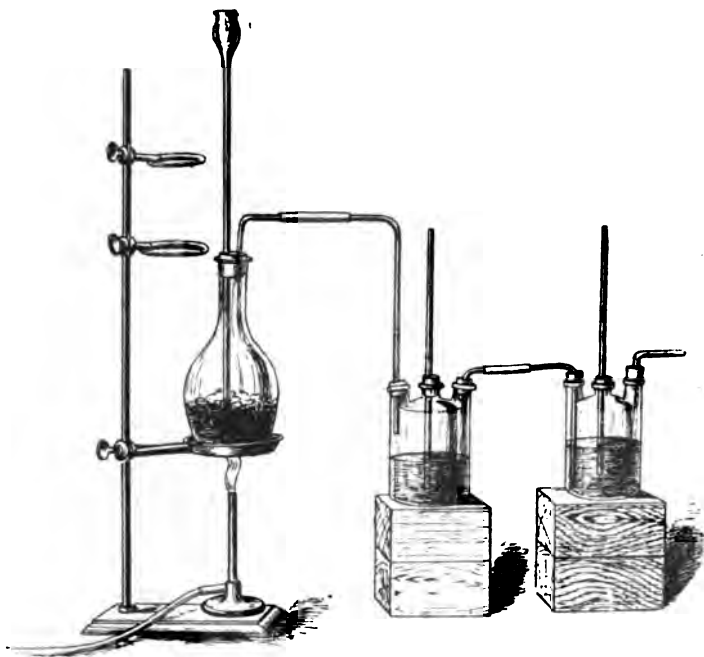


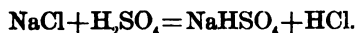
FIG. 7.

Exp. 18. Add to a little chlorine water some solution of indigo or aniline violet. The colors will be discharged.

Immerse a piece of the starch-iodide paper in another portion. It will become blue as explained in the reaction given above.

CHLORINE AND HYDROGEN.

These substances unite directly to form hydrochloric acid. This is, however, commonly prepared by decomposing a chloride by sulphuric acid, as:



Exp. 19. Powder about 25 Gm. of common salt, NaCl, pour it into a flask of 500 to 800 C.c. capacity, and add 30 C.c. of strong sulphuric acid. The flask is furnished with a funnel tube and delivery tube, as shown in Fig. 7. To the delivery tube are attached two Woulfe bottles of about 400 C.c. capacity. Each contains 200 C.c. of water. The delivery tube from the generating flask must not quite reach the water in the first bottle. The tube leading from this dips into the water of the second. The *safety* tubes in the central openings of each bottle must dip into the water and be open at each end.

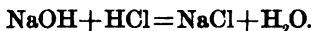
Have the apparatus ready before adding the acid to the salt. When they are mixed the action commences immediately, and continues for some time without application of heat. Finally, place a lamp under the flask and heat gently.

The HCl, which in its pure state is a gas, distils over, and is absorbed largely by the water of the first bottle; what escapes passes into the second and is held there, as it is very soluble in water. After about half an hour remove the lamp and disconnect the bottles. Place the flask in a fume closet, and when cold dissolve out the residue with water.

Test the contents of the bottles as below.

Exp. 20. Immerse in a small portion of the liquid a piece of blue litmus paper. It will turn red. To another portion add a few drops of solution of silver nitrate. A white precipitate forms.

Exp. 21. Take about 100 C.c. of the liquid in the second bottle and add to it with constant stirring a solution of sodium hydrate until an alkaline reaction is just reached; that is until *red* litmus is just turned *blue* by the mixture. Now add a C.c. more of the contents of the second bottle to the mixture, and evaporate it to dryness in a porcelain dish. A white residue will be left, which the taste shows to be common salt.



Commercially, hydrochloric acid is made by heating the salt and acid in large iron retorts, and absorbing the gas in water contained in stone-ware Woulfe bottles.

One volume of water at 0° C. will absorb 503 volumes of the gas. The ordinary commercial acid is, however, much weaker than this.

Fuller details on manufacture, strength and properties of this acid will be given later.

BROMINE.

BROMUM.

Br. 79.8.

Sp. Gr. 3.18.

Bromine occurs chiefly in the waters of salt springs and in the sea. It is a heavy red liquid which vaporizes readily, the vapors being even more irritating than chlorine. It can be obtained from the residue left

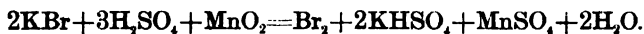
on evaporating the water of the springs where it occurs, after the crystallization of most of the sodium chloride. Two experiments will illustrate the liberation of bromine from such a residue.

Exp. 22. Dissolve a few crystals of potassium bromide in 5 C.c. of water and pass into the solution some chlorine, generated as explained. Note the red color of the liquid due to the free bromine, displaced as shown by this equation.



This test is frequently employed to detect the presence of bromine in a bromide. The second experiment illustrates the reaction employed in working on a large scale.

Exp. 23. Mix two or three Gm. of powdered potassium bromide with an equal weight of manganese dioxide. Place the mixture in a small retort on a sand bath and pour over it a mixture of one part of water and two parts of strong sulphuric acid and apply heat. Bromine is liberated and can be distilled and collected in a cold receiver, and used for the tests below.



On the large scale this process would not yield pure bromine because of the presence of chlorides, and, possibly, iodides in the raw material. When the latter are present they must first be decomposed by the action of a small amount of MnO_2 . Then the main distillation is carried out, and the chlorine present is removed by washing with water and subsequently distilling over solid potassium bromide.

Bromine bleaches as does chlorine, but its action is by no means as powerful. It is somewhat soluble in water, forming a solution known as "bromine water."

Exp. 24. Repeat the bleaching experiments given under chlorine, using bromine water instead.

Bromine imparts to starch paste an orange yellow color, which is characteristic.

Exp. 25. Make a thin starch paste by rubbing a pinch of starch with water to make a cream and boiling it. When cold, add some of the bromine obtained above or a little bromine water. The color fades after a time.

Bromine is used in the direct preparation of many of its compounds. It must be kept in glass-stoppered bottles in a cool place. For shipment these are packed in tin cans with dry earth.

Bromine can be examined for impurities by mixing two or three C.c. with ten times its volume of water, saturating with ammonia water, and making tests for chlorine and iodine as given in the systematic course of analysis in Part III of this book.

IODINE.

IODUM.

L 126.6.

Sp. gr. 4.95.

Iodine exists in sea water, from which it is taken up by plants. These are collected and burned at a low temperature, leaving the iodine combined with potassium, sodium and magnesium as iodides.

It may be liberated, after several preliminary operations, by processes similar to those employed for bromine.

It is a dark gray solid, with a metallic lustre, resembling chlorine and bromine in most of its chemical properties, but weaker. It bleaches, for instance, but only after prolonged action.

It vaporizes readily as shown in this way:

Exp. 26. Heat a small crystal of iodine in a test-tube. A violet vapor is formed which on cooling deposits fine crystals on the upper part of the tube.

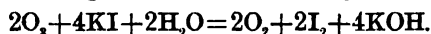
Pour a few C.c. of water in the tube and shake. That a small amount of the iodine has dissolved can be shown by pouring this water over paper smeared with starch paste; a deep blue color forms, due to a combination between the iodine and a portion of the starch.

The above reaction constitutes one of the most delicate tests for both iodine and starch, and in the part of this book relating to volumetric analysis it will be seen that, indirectly, great use can be made of it in other tests and determinations.

Strong *oxidizing* agents as chlorine and ozone can decompose iodides, liberating iodine, as already illustrated for chlorine.

Test-paper, covered with starch paste containing a little potassium iodide, is of great use in the laboratory for showing the presence of such gases.

Exp. 27. Prepare some ozone by the action of moist air on phosphorus, in this way: Scrape a small stick of phosphorus, under water, until it is free from the superficial layer of oxide. Now place it in a beaker in the bottom of which is a small amount of luke-warm water not quite sufficient to cover the phosphorus. Suspend a strip of the test-paper within the beaker and lay a card on top. After a time the paper turns blue as the generated ozone decomposes the iodide:



Notice at the same time the peculiar odor of this gas.

Test-papers prepared by covering good book-paper with a paste of

Water.....	1000 parts
Starch.....	50 "
Potassium iodide.....	5 "

and drying in an atmosphere free from oxidizing gases, form the so-called Schönbein test for the presence of ozone in the air. The paper is cut in small strips (2 Cm. by 10), moistened in pure water and suspended in the air. If a blue color appears it shows the presence of ozone or some other strong oxidizing gas.

Iodine is used in the direct preparation of several of its compounds.

It should volatilize completely, dissolve in alcohol, carbon bisulphide, chloroform, and solution of potassium iodide, without residue. It should not show more than traces of bromine or chlorine when examined by methods to be given later.

TINCTURE OF IODINE.

TINCTURA IODI.

Iodine..... 80 Gm.
Alcohol..... 920 Gm., or 1,135 C.c.

Reduce the iodine to a coarse powder by trituration. Then add it to the alcohol in a glass stoppered bottle. Set the mixture in a warm place, and occasionally agitate the bottle until the iodine is dissolved.

Notes.—The powdering of the iodine and putting the mixture in a warm place hasten the otherwise slow solution.

Tests.—The standard solution of sodium thiosulphate, described later, should show 8 per cent. of iodine.

COMPOUND SOLUTION OF IODINE.

LIQUOR IODI COMPOSITUS.

LUGOL'S SOLUTION.

Iodine..... 50 Gm.
Potassium iodide..... 100 Gm.
Distilled water..... 850 C.c.

Dissolve the iodine and iodide in the water.

Keep the solution in a glass stoppered bottle.

Tests.—The thiosulphate solution should show 5 per cent. of iodine.

IODINE LINIMENT.

LINIMENTUM IODI; B.

Iodine..... 50 Gm.
Potassium iodide..... 20 Gm.
Glycerin..... 10 Gm.
Rectified spirit..... 400 C.c.
Dissolve.

DECOLORIZED TINCTURE OF IODINE.**TINCTURA IODI DECOLORATA.**

Iodine.....	40 Gm.
Alcohol.....	400 C.c.
Stronger water of ammonia.....	90 C.c.

Powder the iodine by trituration. Dissolve it in the alcohol. Add the ammonia water carefully without shaking or stirring the mixture.

Let the mixture stand exposed to sunlight until decolorized, which will require from a few days to several weeks.

Notes.—As explosive nitrogen iodide is liable to be produced when the ammonia is added to the iodine solution, any dark-colored sediment formed in the liquid should warn the operator to leave the mixture at perfect rest until the precipitate has disappeared, which it will finally do. If a few drops of phenol be added to the mixture it becomes decolorized at once.

The preparation contains not iodine, but ammonium iodide and ethyl iodide.

IODIZED STARCH.**AMYLUM IODATUM.**

Iodine.....	1 Gm.
Starch.....	19 Gm.
Distilled water, sufficient.	

Triturate the iodine with a little distilled water; add the starch gradually and continue the trituration until the compound assumes a uniform blue color, approaching black. Dry at a temperature not exceeding 40° C. (104° F.) and then powder it.

Notes.—A partial chemical union takes place.

Iodized starch should be kept in glass stoppered bottles.

IODIZED STARCH PASTE.**GLYCERITUM AMYLI IODATUM.**

Starch.....	10 Gm.
Glycerin.....	20 C.c.
Water.....	60 C.c.
Compound solution of iodine.....	10 C.c.

Boil the starch, glycerin and water together, stirring constantly, until a homogeneous semi-transparent paste is formed; then remove it from the source of heat, and, when nearly cold, mix it with the iodine solution.

GLYCERITE OF IODINE.**GLYCERITUM IODI.**

Iodine.....	4 Gm.
Glycerin.....	96 C.c.

Triturate the iodine with a portion of the glycerin until reduced to a smooth paste; then gradually add the remainder of the glycerin and heat the mixture carefully by water-bath until solution is effected.

Notes.—Some chemical reaction occurs, so that the product is not wholly a simple solution.

CARBOLIZED IODINE SOLUTION.**LIQUOR IODI PHENOLATUS.**

Tincture of iodine.....	1 Gm.
Phenol.....	12 Centigrams.
Glycerin.....	8 Gm.
Water.....	45 C.c.
Mix.	

A colorless liquid is obtained.

IODIZED OIL.**OLEUM IODATUM.**

Iodine.....	1 Gm.
Paraffin oil.....	30 C.c.

Triturate the iodine with a small portion of the oil until reduced to a smooth paste, and then dissolve by the aid of heat.

FLUORINE.**FLUORUM.**

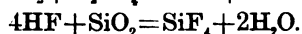
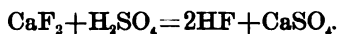
F. 19. Sp. gr. ———

Fluorine occurs chiefly in calcium fluoride (fluor-spar) and in sodium aluminium fluoride (kryolite).

It is not known in the free state. From fluor-spar hydrofluoric acid can be liberated for etching glass, which is illustrated in this way:

Exp. 28. Make a paste by stirring powdered fluor-spar with strong sulphuric acid in a lead dish. Cover a piece of glass with a

thin layer of melted beeswax and scratch through this a design to be etched. Support the glass over the dish, but not in immediate contact with it. Apply a gentle heat to the dish, but not strong enough to melt the wax above. After ten or fifteen minutes remove the plate, and melt off the wax. The exposed part has been corroded by the liberated hydrofluoric acid:



Glass contains *silica*, SiO_2 , which is attacked, forming volatile silicon fluoride and water, as shown by the equation.

CHAPTER III.

NITROGEN.

NITROGENIUM.

N. 14.

Sp. gr. ($n-1$) 14.

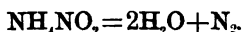
Nitrogen is found free in the atmosphere, of which it makes up 77.01 per cent. Combined, it occurs in animal and vegetable tissue and in several minerals. It can be obtained from the air by taking away the oxygen by appropriate means.



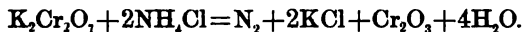
FIG. 8.

Exp. 29. Enclose a piece of phosphorus, about the size of a small pea, in a cage of wire gauze. Place this in a capsule, which floats on the water in a large dish, as shown in Fig. 8. Ignite the phosphorus and depress over it a bell-jar or wide mouthed bottle so that the air is completely enclosed. The oxygen combines with the phosphorus, and water ascends to fill its place. By closing the mouth of the bottle or jar with a glass plate it can be inverted without losing the gas. A lighted splinter plunged in this will be extinguished.

Pure nitrogen can be obtained by heating a strong solution of ammonium nitrite, NH_4NO_2 , which decomposes in this way:



For this salt a mixture of NH_4Cl and KNO_3 can be substituted. Another practical method is illustrated by this equation:



Exp. 30. Mix about six Gm. of powdered potassium bichromate with half its weight of ammonium chloride. Charge a tube, such as is used for generation of oxygen and shown in Fig. 1, with this mixture, and apply heat. The nitrogen can be collected in bottles over water and tested, so as to show its negative properties. It is not combustible, nor will it support combustion.

NITROGEN AND OXYGEN.

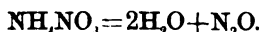
Nitrogen combines with oxygen to form five compounds, which are named as follows:

Nitrogen monoxide	N_2O	gas.
Nitrogen dioxide	N_2O_2	gas.
Nitrogen trioxide	N_2O_3	volatile liquid.
Nitrogen tetroxide	N_2O_4	volatile liquid.
Nitrogen pentoxide	N_2O_5	solid.

The preparation of the first and second of these will be shown by experiment.

Exp. 31. Dry a small flask, holding about 150 C.c. and place in it 10 or 15 Gm. of *dry* ammonium nitrate, NH_4NO_3 . By a delivery tube connect this flask with a receiving bottle standing over water, as shown in Fig. 9. Apply heat, and notice that the flask becomes filled with vapor and white fumes, while bubbles of gas ascend through the water. When the air has been expelled collect several bottles of the gas and test it.

It is the so-called *laughing-gas*, and has a pleasant smell and taste. The reaction by which it is liberated is:



Exp. 32. Test bottles of the gas by burning in them phosphorus, charcoal and sulphur as described under oxygen. It is an active supporter of combustion.

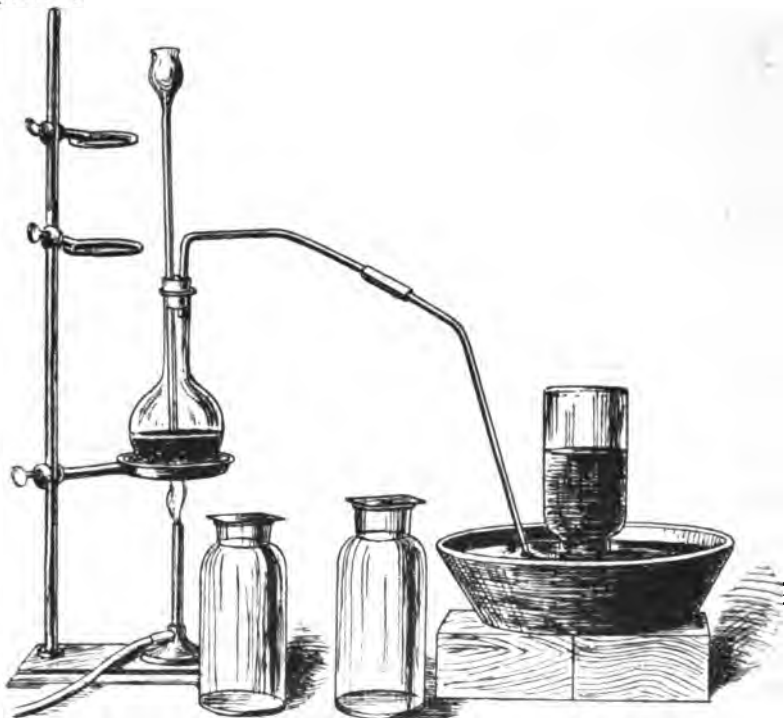
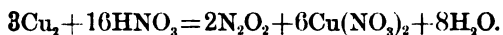
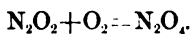


FIG. 9.

The nitrogen dioxide, N_2O_2 , can be made by the action of strong nitric acid on several metals. Copper is usually employed, when the reaction is as follows:



Exp. 33. Arrange a bottle as for generating hydrogen by action of dilute sulphuric acid on zinc, and charge it with about 20 Gm. of copper turnings and 25 C.c. of water. Pour in now through the funnel tube 25 to 50 C.c. of strong nitric acid. At first red fumes fill the bottle; when these have been driven out connect with a receiving bottle over water, and collect as directed for hydrogen. This experiment should be tried where there is a good circulation of air, as the gas, or rather the product which it forms with oxygen, is very irritating.



The N_2O_2 is colorless, but the N_2O_4 is red. When most of the heavy metals are treated with strong nitric acid, the reaction given above takes place; but in the air the liberated N_2O_2 combines immediately to form N_2O_4 .

Nitrogen trioxide is a blue volatile liquid, and may be prepared, mixed with other oxides, by the action of a strong nitric acid on starch.

Nitrogen tetroxide can be readily made by strongly heating dry lead nitrate:



The oxide may be condensed by a freezing mixture to a greenish yellow liquid.

Nitrogen pentoxide may be prepared by action of phosphoric oxide on anhydrous nitric acid:

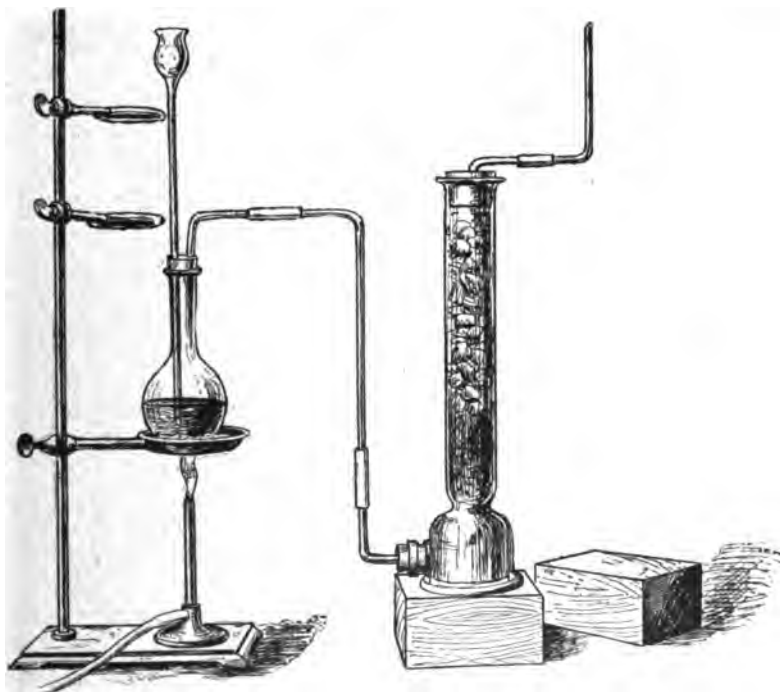
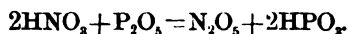


FIG. 10.

NITROGEN AND HYDROGEN.

These elements may be directly combined by the agency of electricity, forming ammonia, NH_3 . The same compound is readily obtained by boiling its strong solution in water, the ordinary *ammonia water* or *aqua ammoniac*.

Exp. 34. Arrange the apparatus as shown in the adjoining figure. The flask holding about 250 C.c. contains 50 C.c. of strong ammonia water; the cylinder is filled with lumps of freshly burned lime. By applying heat the ammonia gas is driven out, carrying with it a little water vapor. The latter is absorbed on coming in contact with the lime, and dry NH_3 escapes from the upright tube. This being lighter than air can be collected by upward displacement. (See Fig. 10.)

Exp. 35. Fill a large test-tube with the gas, close it with the thumb, and dip the lower end in water. Now remove the thumb, when the water will rush up and nearly, or quite, fill the tube. This is due to the rapid absorption of the gas, one volume of water being capable of absorbing at 0°C . about 1,000 volumes of the gas.

The preparation of ammonia water from the raw material is illustrated by the next experiment.

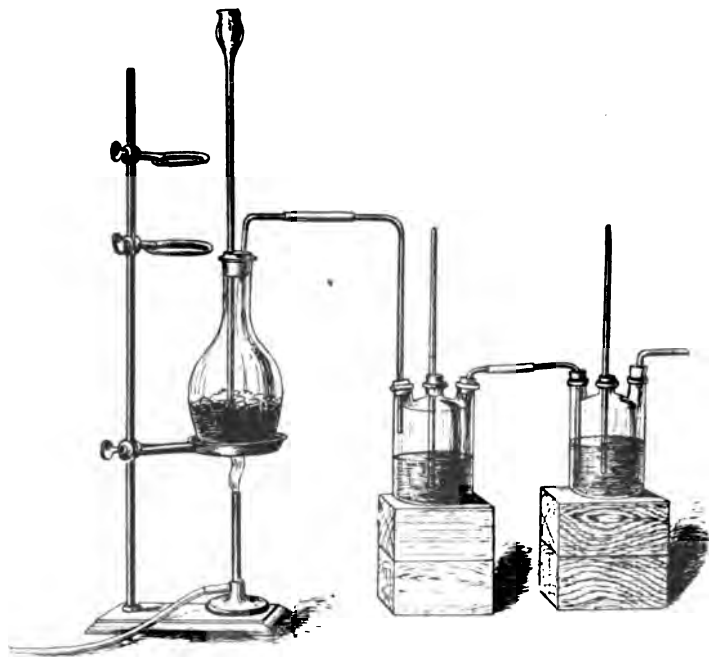
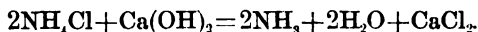


FIG. 11.

Exp. 36. Mix equal weights of ammonium chloride and good slaked lime, about 20 Gm. of each, and heat in a flask of about 250 C.c. capacity, connected by a delivery tube with two Woulfe bottles, as described for the generation and absorption of hydrochloric acid. The gas and water vapor are liberated according to the following equation, and pass over to be absorbed by the water in the bottles (See Fig. 11):

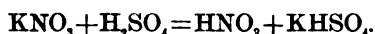


The presence of ammonia in the water is shown by the smell, and reaction with red litmus paper, which is turned blue.

On a large scale this reaction is carried out by heating the mixture in iron or stone-ware retorts.

NITROGEN, HYDROGEN AND OXYGEN.

These three elements combine to form several acids, only one of which is of practical importance. This is nitric acid, HNO_3 , and is made by the action of strong sulphuric acid on potassium nitrate:



Exp. 37. The reaction can be illustrated on a small scale by heating 50 Gm. of powdered potassium nitrate and a somewhat greater weight of strong sulphuric acid in a retort of 200 or 300 C.c. capacity, such as shown in Fig. 12. The liberated HNO_3 passes over and is condensed in the receiver, which must be kept cold by pouring on water.

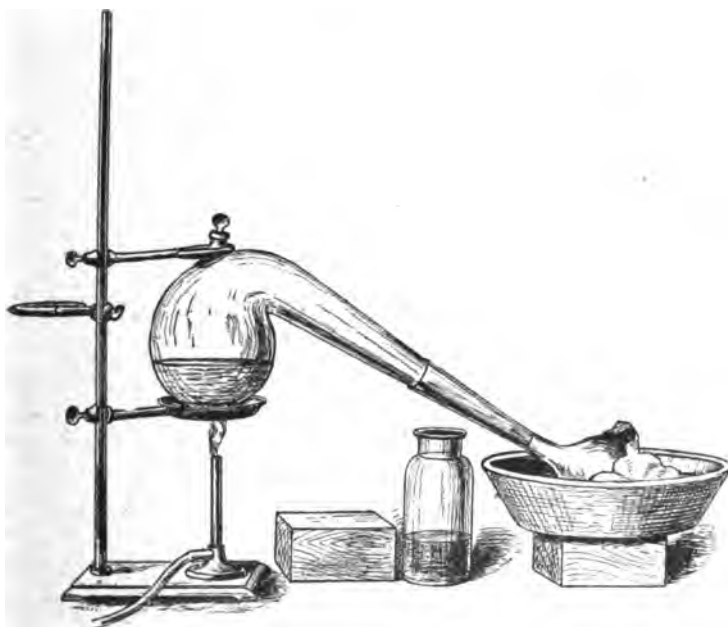
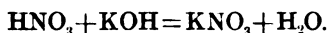


FIG. 12.

Exp. 38 and 39. Test a little of the acid with blue litmus paper, which is thereby turned red. Now add to a somewhat larger portion solution of potassium or sodium hydrate until it no longer turns blue litmus paper red, and evaporate the mixture so obtained to dryness in a porcelain dish. The result is potassium or sodium nitrate, according to the reaction.



In most cases, by the action of nitric acid on an alkaline hydrate or on a metal, a *nitrate* is produced. In a few instances, however, this is not true, as shown by the following experiment:

Exp. 40. To the remainder of the acid made above add about half a Gm. of powdered antimony and boil in a porcelain dish. The metal does not dissolve, but is converted into a white insoluble powder, consisting of antimonious oxide Sb_2O_3 . With metallic tin a similar reaction would take place.

AQUA REGIA.

By mixing one volume of strong nitric acid with about three volumes of strong hydrochloric, a liquid known as *aqua regia* is obtained. This is capable of dissolving a number of metallic substances and oxides which either one of the acids alone will not act upon. The two react on each other, liberating chlorine and nitrosyl chloride as shown in this equation:



Further details will be found later.

NITROGEN AND IODINE.

Chlorine, bromine and iodine combine with nitrogen forming very explosive compounds. The compound of nitrogen and iodine can be made in small amount, without danger, as follows:

Exp. 41. Powder a few crystals of iodine in a porcelain dish and pour over it a little strong ammonia water. In twenty minutes pour this off and by means of water wash the dark powder into several small filters and there wash with more water. Then hang the papers up to dry. On touching the powders now with a glass rod, or piece of paper even, they explode with a sharp report.

SULPHUR.

SULPHUR.

S. 32.

Sp. gr. 1.96—2.05.

Sulphur occurs in the free state in volcanic regions, and widely distributed in the form of sulphides and sulphates of metals.

The sulphur of commerce is obtained from the native sulphur by melting to free it from accompanying earthy matters, or from ferric sulphide, FeS_2 , commonly called *iron pyrites*, by distillation.

It exists in several modifications, having different crystalline structures and different specific gravities. The melting point is 115°C .

Exp. 42. Melt some sulphur in a wide test-tube, and observe that it forms a light yellow liquid. On further heating it becomes thicker and darker, almost black, but at a still higher temperature becomes thinner again.

It boils at a temperature of 448° C. If heated to this point the dark liquid is converted into an amber-colored vapor. By pouring now the contents of the tube into water a plastic brown mass is obtained, which in several physical properties resembles rubber. It is quite elastic, and can be drawn out into fine threads.

On standing, however, it returns to the hard, brittle form.

Ordinary sulphur appears in commerce as "roll" sulphur ("brimstone"), or as "sublimed" sulphur.

SUBLIMED SULPHUR.

SULPHUR SUBLIMATUM.

This is a fine lemon yellow powder having a peculiar, faint odor and taste, and a slightly acid reaction from the presence of sulphuric acid, with which it is more or less contaminated. It may contain a little arsenic. It is insoluble in water and alcohol.

WASHED SULPHUR.

SULPHUR LOTUM.

Sublimed sulphur.....	1,200 Gm.
Ammonia water.....	100 C.c.
Water, sufficient.	

Add the sulphur to 1,200 C.c. of water previously mixed with the ammonia water, and digest for three days, agitating occasionally. Then add 1,200 C.c. of water, transfer the mixture to a muslin strainer, and wash the sulphur with water until the washings cease to produce a precipitate in test solution of barium chloride. Then drain, press strongly, dry it at not over 40° C. (104° F.), and powder by running it through a No. 80 sieve.

Notes.—The object of this process is to neutralize and wash away the sulphuric acid which is always present with sublimed sulphur, and the digestion for three days is intended to remove also any arsenic present. To effect the extraction of the arsenic, continued digestion is required, and three days is not too long, as the ammonia is very diluted. Care should be taken, however, not to use higher heat than 40° C. (104° F.), because above that temperature a good deal of ammonium sulphydrate may be formed, and at the boiling point the sulphur will dissolve as long as sufficient ammonia remains to act upon it. Boiling water is, therefore, not to be used. It is under all circumstances necessary to wash out all the ammonia and ammonium salt from the sulphur before drying it.

It is important to dry the washed sulphur thoroughly before putting it in its receptacle, for the presence of any moisture would result in the formation of sulphuric acid again, rendering a repetition of the washing necessary.

Description.—It is a light yellow powder, somewhat paler than sublimed sulphur, without odor and nearly tasteless. It is insoluble in water and alcohol, and should leave no residue on volatilization.

Tests.—Digest a few Gm. with pure water and test with blue litmus paper. It should not redden, showing absence of free acids. Digest 20 Gm. with pure ammonia water and filter. The filtrate should show absence of arsenic compounds by tests described later.

PRECIPITATED SULPHUR.

SULPHUR PRÆCIPITATUM.

Sublimed sulphur 2 parts.
Lime 1 part.
Hydrochloric acid, water, each sufficient.

Slake the lime and make it into a uniform mixture with 10 parts of water. Add the sulphur, previously well dried and sifted, mix well, add 25 parts of water, and heat the mixture to boiling for one hour, stirring constantly, and replacing the water lost by evaporation. Then cover the vessel, allow the contents to cool, pour off the clear solution, filter the remainder, and unite the liquids. Add gradually hydrochloric acid previously diluted with an equal volume of water, until the liquid is nearly neutralized, being careful to leave it still distinctly alkaline in reaction. Collect the precipitate on a strainer, and wash it with water until the washings are tasteless. Then dry it at a gentle heat.

Reactions.—The lime is first slaked, $\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$. Then, when sulphur is boiled with the calcium hydrate, the following reaction occurs: $3\text{Ca}(\text{OH})_2 + 6\text{S}_2 = 2\text{CaS}_3 + \text{CaS}_2\text{O}_3 + 3\text{H}_2\text{O}$. The solution, containing calcium sulphide and calcium thiosulphate, is next treated with hydrochloric acid, when sulphur is precipitated: $2\text{CaS}_3 + 4\text{HCl} = 2\text{CaCl}_2 + 4\text{S}_2 + 2\text{H}_2\text{S}$.

Notes.—The quantity of lime used is purposely somewhat in excess of the amount required by theory, to make up for carbonate contained in it. A larger excess would, however, result in loss because the lower sulphides of calcium then formed would yield larger quantities of H_2S when the hydrochloric acid is added.

If the first portion of hydrochloric acid is added very slowly no hydrogen sulphide is formed, because the reaction then is: $2\text{CaS}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{Ca}(\text{SH})_2 + 4\text{S}_2$. When more acid is added, however, the reaction just described is followed by: $\text{Ca}(\text{SH})_2 + 2\text{HCl} = \text{CaCl}_2 + 2\text{H}_2\text{S}$.

The directions of the Pharmacopœia of the United States are to only “nearly” neutralize the solution, and to be careful to leave it slightly *alkaline*. The object of this precaution is to prevent the precipitation of any arsenic present. The calcium thiosulphate is not decomposed unless enough hydrochloric acid be added to impart an acid reaction to the liquid. Hence the sulphur which enters into the structure of the calcium thiosulphate is lost. But if enough hydrochloric

acid be added to decompose the thiosulphate ($2\text{CaS}_2 + \text{CaS}_2\text{O}_3 + 6\text{HCl} = 3\text{CaCl}_2 + 6\text{S}_2 + 3\text{H}_2\text{O}$), the arsenic will also be precipitated, as follows: $\text{Ca}_2(\text{AsS}_4)_3 + 6\text{HCl} = \text{As}_2\text{S}_3 + 3\text{H}_2\text{S} + 3\text{CaCl}_2$.

When the liquid is alkaline, however, all of the arsenic remains in solution.

Care should be taken to arrange so that the hydrogen sulphide gas is led off through a flue, or the operation should be carried out in the open air. The gas is evolved in large enough quantities to be very annoying to the operator.

The acid must be added to the solution of calcium sulphide and not *vice versa*; moreover, the acid must be diluted as directed; otherwise an oily product (H_2S_2 ?) is formed which afterwards is difficult to eliminate and which but slowly decomposes, giving off H_2S .

So-called "milk of sulphur" is precipitated sulphur made by a process similar to the one above described, with the exceptions that sulphuric acid is used instead of hydrochloric acid, and that the acid is added in excess in order to decompose the calcium thiosulphate as well as the sulphide, thus throwing down all the sulphur. But this also precipitates a large quantity of calcium sulphate, which thus constitutes a considerable proportion of the "lac sulphuris," rendering it unfit for use.

Description.—This is a fine yellowish white powder resembling in chemical properties the other forms described.

It is to be preferred to both the washed and sublimed sulphur for most purposes in pharmacy, especially in mixtures, ointments, powders and confections, because of its extremely fine state of division.

Tests.—The absence of free acid or arsenic compounds should be determined as under the last head. It should be completely volatile. This would show the absence of calcium sulphate. This can be further shown by boiling a few Gm. with dilute hydrochloric acid, filtering and dividing the filtrate into two parts. One part tested with barium chloride solution should give no precipitate of sulphate, and the other part treated with ammonia water and ammonium oxalate should give no precipitate of calcium oxalate.

SULPHURATED OIL.

OLEUM SULPHURATUM.

Sublimed sulphur 1 part.
Flaxseed oil 6 parts.

Boil together in a capacious vessel, stirring constantly, until solution is effected.

Notes.—High heat is necessary, and there is danger that the mixture may boil over unless the vessel is large enough and the process guarded.

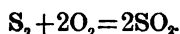
Description.—The product is a thick, reddish brown, oily liquid, having a nauseous odor. It is wholly soluble in oil of turpentine.

SULPHUR AND OXYGEN.

Sulphur forms two compounds with oxygen: sulphurous anhydride, SO_2 , and sulphuric anhydride, SO_3 .

The first is readily prepared by burning sulphur in the air, and is used in large quantities in the manufacture of sulphuric acid, in bleaching, and in fumigation.

Exp. 43. Place a piece of sulphur as large as a pea in a deflagrating spoon, heat it in a lamp flame until it ignites, and then plunge it in a bottle of 300 or 400 C.c. capacity. The sulphur burns at the expense of the oxygen of the air in the bottle, leaving SO_2 .



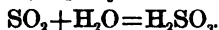
Fill several bottles in this way, cover them with glass plates, and test as below.

Exp. 44. Moisten a piece of calico in water and suspend it in one of the bottles; after a time it becomes bleached. Sulphur bleaching differs from chlorine bleaching in this respect, that with the latter there is a destruction of the colored compound, while with the former there is a union with the colored compound, producing a colorless one. The addition of a stronger acid, by liberating the SO_2 , usually restores the color.

Exp. 45. Add some water to a second bottle and shake. Then add solution of potassium permanganate, and note the disappearance of its color.

To another bottle add considerable water, shake well, and then add tincture of iodine or solution of iodine in potassium iodide. The color disappears here, as before. In both cases the SO_2 acts as a strong reducing agent, converting the colored bodies into others without color.

These reactions will be taken up again. The solution of the gas in water forms sulphurous acid, H_2SO_3 :



The union is not permanent, as application of heat easily separates the water and gas.

SULPHUR AND HYDROGEN.

Two compounds are known here: hydrogen mono-sulphide (ordinary hydrogen sulphide or sulphuretted hydrogen) H_2S , and hydrogen disulphide, H_2S_2 . The first is easily prepared.

Exp. 46. Arrange a bottle as for making hydrogen. Place in it 20 Gm. of ferrous sulphide, FeS , in small lumps; cover this with water and add through the funnel tube a few C.c. of strong HCl . Gas bubbles escape from the liquid, and, mixed with air, pass out through the delivery tube. Pass the first portions of the gas into water, and notice that this speedily acquires its peculiar odor.

Exp. 47. Prepare dilute solutions of copper sulphate, zinc sulphate and potassium-antimony tartrate in water. Add to the second and third a few drops of acetic acid, and allow the gas to bubble through each one in turn.

From the copper solution a black precipitate is thrown down, from the zinc solution a white, and from the antimony solution an orange yellow one. These precipitates are *sulphides* of copper, zinc and antimony, and illustrate the most important property of the gas. When discussing the tests of Qualitative Analysis this will be fully explained.

CHAPTER IV.

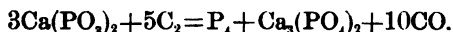
PHOSPHORUS.

PHOSPHORUS.

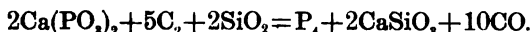
P. 31.

Sp. gr. 1.83.

Phosphorus occurs chiefly as calcium phosphate, a constituent of bones, and also a mineral, *apatite*. The free substance is made from bone-ash or the native phosphate by converting it first into acid calcium phosphate, then into calcium metaphosphate, which is heated in retorts with charcoal. The phosphorus distills and is condensed under water. The final reaction is:



If sand is added with the charcoal the reaction is this:



It is a clear, light yellow waxy substance, insoluble in water, but soluble in carbon bisulphide, ether and oils. It melts at 44°C . It must be kept under water, as in the air it combines so readily with oxygen as to inflame spontaneously.

Large quantities of it must be kept under water in sealed tin cans.

Common phosphorus is never quite pure. It can be best tested by oxidizing it to phosphoric acid by means of nitric acid (equal parts of strong acid and water), diluting the solution so obtained with water, and applying tests for sulphates (from sulphur) and arsenates (from arsenic) to be given later. Not more than a trace of either should be shown.

AMORPHOUS PHOSPHORUS.

By heating ordinary phosphorus in a vacuum or in an atmosphere of carbon dioxide to a temperature of 240°C ., it is converted into a

modification known as red phosphorus. This is different from the common phosphorus in most properties. It is insoluble in the liquids which dissolve the other, is not poisonous, and is not oxidized at ordinary temperatures. Above 280° C. it reverts to the common form.

Exp. 48. Heat a little red phosphorus in a narrow glass tube sealed at the lower end. A light yellow deposit forms in the upper part of the tube. This is common phosphorus, as can be shown by breaking off the closed end of the tube and heating gently.

SOLUTION OF PHOSPHORUS.

Phosphorus being slightly soluble in alcohol, a solution called "tincture of phosphorus" has been prepared by dissolving it in 500 parts of hot alcohol and diluting to 1,000 parts. Such a solution is of limited use, as it precipitates on addition of water.

GRANULATED PHOSPHORUS.

Phosphorus	5 Gm.
Sodium chloride	25 Gm.
Distilled water	100 C.c.

Dissolve the sodium chloride in the water contained in a bottle of the capacity of 200 C.c.; add the phosphorus in small shavings. Warm in a water-bath until the phosphorus melts. Then shake it until cold. Pour off the salt solution, and wash the phosphorus with distilled water several times.

Preserve it in a bottle under water. Used for making pills.

PHOSPHORATED OIL.

OLEUM PHOSPHORATUM.

Phosphorus	1 Gm.
Stronger ether	12 C.c.
Expressed almond oil, sufficient.	

Introduce about 100 C.c. of almond oil into a flask, and heat it for fifteen minutes on sand-bath at 250° C. (482° F.). Allow it to cool, and then filter. Put 90 C.c. of the filtered oil together with the phosphorus, previously well dried by gently touching it with blotting paper, into a dry and tared four-ounce bottle; insert the stopper and heat the bottle in a water-bath until the phosphorus melts; shake until dissolved; let cool and then add the stronger ether. Now take the weight of the contents of the bottle and add enough of the prepared oil of almond to make the weight of the final product 100 Gm.

Notes.—Keeping the oil of almond at the high temperature prescribed for fifteen minutes expels moisture and air from it, and also causes the separation of

some organic matters which deposit in the form of a flocculent sediment on cooling and are then filtered out. The oil thus prepared is nearly colorless.

The phosphorus used should be a clean, translucent section.

Ether must not be used in place of stronger ether, as the preparation would then be unclear.

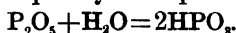
The product should be kept in one-ounce, amber colored, glass stoppered bottles, and in a cool place. At a too low temperature the phosphorus crystallizes out; this should be carefully guarded against, and when it occurs it should not escape observation. The separated phosphorus may be readily redissolved by gently warming and shaking.

PHOSPHORUS AND OXYGEN.

Phosphorus forms two oxides: the trioxide, P_2O_3 , and the pentoxide, P_2O_5 . The preparation of the second has been illustrated already. It is a light white powder, which can be made and examined as follows:

Exp. 49. Dry a piece of phosphorus as large as a small pea, by means of blotting paper, place it in a small porcelain crucible resting on an iron plate; apply heat to ignite it, and then place a dry, clean bottle, mouth down, over the crucible. The phosphorus burns at the expense of the oxygen in the bottle, which becomes filled with white fumes of P_2O_5 .

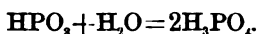
If, when the action has ceased, a little water is poured in the bottle, it unites with the oxide so quickly as to produce a hissing noise:



This P_2O_5 is useful in drying gases, because of its very strong affinity for moisture.

With cold water it produces metaphosphoric acid, as just shown.

When the solution is boiled more water is taken up, giving orthophosphoric acid:



PHOSPHORUS AND HYDROGEN.

Phosphorus forms several compounds with hydrogen. The preparation of one of these is illustrated in the following experiment:

Exp. 50. Arrange the apparatus as shown in Fig. 13. In the flask of 200 C.c. capacity pour about 150 C.c. of solution of potassium or sodium hydrate. Then drop in a piece of phosphorus, the size of a small pea, and add a few drops of ether. Close the flask with the cork and delivery tube and apply heat. The ether drives out the air from the top of the flask. The phosphorus acts on the alkali, liberating gaseous hydrogen phosphide, PH_3 , which escapes from the delivery tube, the end of which is just beneath the surface of the water in the dish represented.

As soon as the gas comes in contact with the air it burns spontaneously, forming phosphorus pentoxide, which ascends in rings of white fumes. The reaction in the flask is this:

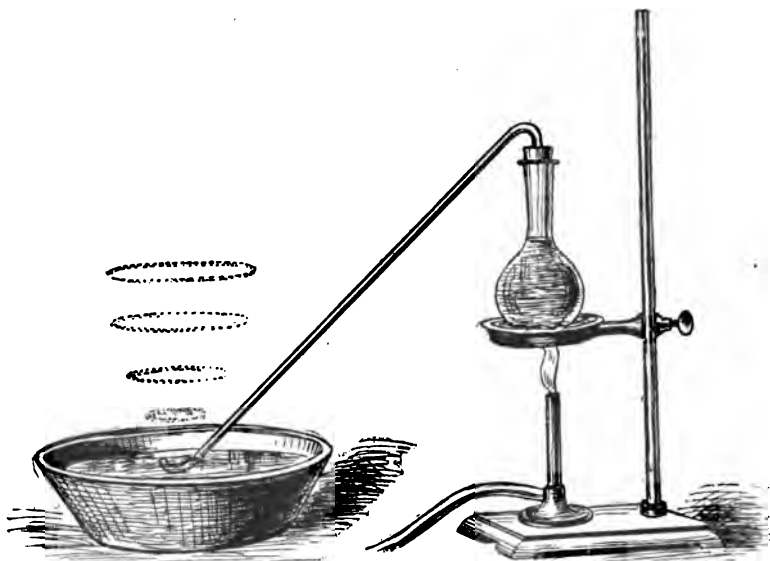
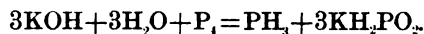


FIG. 13.

If the gas is passed through a freezing mixture before reaching the air it ceases to be spontaneously inflammable, as this operation takes out a *liquid* hydrogen phosphide, the cause of the inflammability. The pure PH_3 has a peculiar and disagreeable odor. It is poisonous.

BORON.

BORON.

B. 11.

Sp. gr. 2.68.

Boron occurs in boric acid and borax (sodium baborate); also in a few less important compounds. The free element can be obtained in two forms, amorphous and crystalline, by several processes. It has no practical value.

SILICON.

SILICON.

Si. 28.

Sp. gr. 2.49.

Silicon always occurs with oxygen, and after the latter, is the most abundant element of the earth's crust. The common mineral *quartz* is

oxide of silicon, SiO_2 . This combines with metallic oxides, forming silicates, as felspar, mica, the clays, etc.

The element can be obtained by laboratory processes, but has no commercial use.

CARBON.

CARBONEUM.

C. 12.

Sp. gr. (diamond) 3.01–3.25.

Carbon occurs free in several forms; as the diamond, as graphite, as coal, and in artificial products such as lamp-black, soot, charcoal, coke, and gas carbon. In combination carbon is abundant. It is found

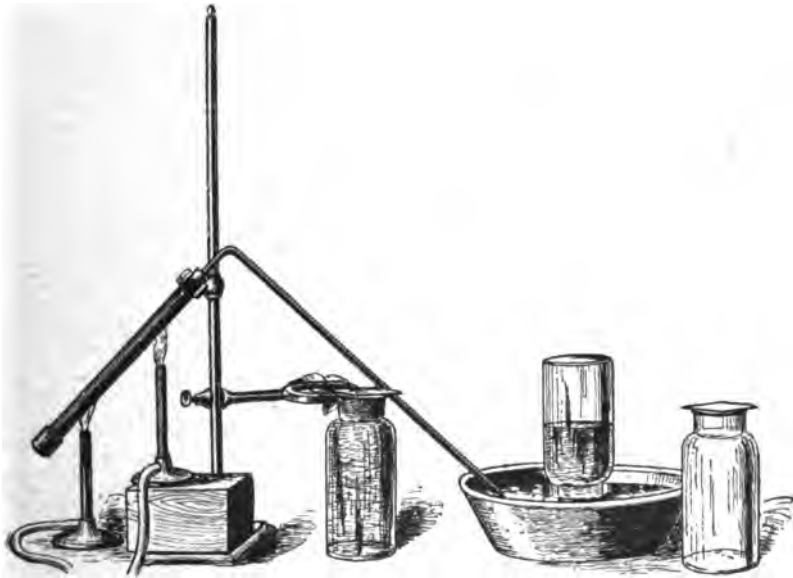


FIG 14.

in the air as carbon dioxide, and in the earth's crust in various carbonates. Calcium carbonate or lime-stone is the most important of these. Charcoal is obtained from wood, and coke from coal by a process of destructive distillation illustrated in the following experiments:

Exp. 51. Charge a small retort, consisting of a piece of iron gas-pipe 20 Cm. long and 15 Mm. in internal diameter, and closed airtight at one end by an iron plug, with shavings or fine splinters, and attach it to a delivery tube and receiver as shown in Fig. 14.

Heat strongly with a Bunsen burner. The wood is decomposed and a mixture of water, acid liquids and gas passes over. The gas collects in the bottle while the other substances condense.

When the evolution of the gas has ceased, withdraw the delivery tube and then remove the lamp. After the iron tube has cooled shake out the contents, or remove them with a bit of wire, and test by burning.

Close the mouth of the bottle with a glass plate, invert it and open to the air and apply a match. The gas burns with a bright flame.

Exp. 25. Repeat the last experiment, using soft coal, in small lumps, instead of wood. *Coke* remains in the tube, while a gas, similar to ordinary illuminating gas, collects in the bottle, and can be tested as before.

Several varieties of charcoal can be briefly mentioned here. By

CHARCOAL,

CARBO LIGNI,

is meant the ordinary wood product, prepared best from willow or poplar, as these give the lightest and most porous kinds. Other woods are also used.

ANIMAL CHARCOAL.

CARBO ANIMALIS,

usually made from bones.

Dull, black, granular fragments, or powder, odorless, nearly tasteless, insoluble in water and alcohol. When ignited it leaves a white residue consisting of *bone-ash*, a mixture of calcium phosphate and carbonate chiefly. This should make up at least 86 per cent. of the original weight, and be completely soluble in hydrochloric acid. The bone charcoal has a remarkable power of absorbing many organic substances, as shown in this experiment.

Exp. 53. Pack a filter loosely with the animal charcoal, and pour on a solution of logwood, cochineal or litmus. A clear or nearly clear liquid will run through. It may be necessary to pour a second or third time to remove all the color.

Animal charcoal is frequently employed in decolorizing solutions of alkaloids or other organic substances; but there is usually a loss here, as it likewise holds some of the latter.

On a large scale it is used in sugar-houses for clarifying syrups and solutions for evaporation.

PURIFIED ANIMAL CHARCOAL.

CARBO ANIMALIS PURIFICATUS.

Animal charcoal, in fine powder.....	500 Gm.
Hydrochloric acid.....	620 C.c.
Water, sufficient.	

Mix the acid with 1,250 C.c. of water, pour the mixture over the animal charcoal, and digest in water-bath for twenty-four hours, stirring occasionally. Decant the liquid and digest the residue with 1,500 C.c. of water for two hours. Transfer the mixture to a strainer, let it drain, and then wash the residue with water until the washings cease to precipitate or color silver nitrate solution. Dry the product, heat it to low redness in a covered crucible, and when cool transfer to bottles and keep tightly stoppered.

Description.—It is a dull black powder which gives nothing to water or alcohol; on ignition with oxygen it should leave only a trace of residue.

The solution obtained by heating with dilute hydrochloric acid, and filtering, should give no test for phosphates.

CARBON AND OXYGEN.

Carbon forms two compounds with oxygen, the *monoxide*, CO, and the *dioxide*, CO₂. Both are gases.

Exp. 54. Powder 10 or 15 Gm. of potassium ferrocyanide, K₄Fe(CN)₆, place it in a flask of 300 C.c. capacity having a funnel tube and delivery tube. Add ten times its weight of strong sulphuric acid and heat gently on a sand-bath. The delivery tube should pass under water. Carbon monoxide is given off when a sufficiently high temperature is reached, and may be collected in bottles as with hydrogen. Care must be taken to avoid applying too much heat, as the reaction would become very violent, and it should be remembered that the gas must not be inhaled, as it is very poisonous.

The contents of the bottle can be tested by applying a match. The gas burns with a blue flame, CO₂ being formed.

By removing the delivery tube from the water and replacing it with one drawn to a point, the gas may be burned directly.

The reaction which takes place is represented by this equation:



The 6 molecules of water come from the crystallized ferrocyanide itself, and from the commercial acid employed.

Carbon monoxide is but slightly soluble in water, and can be liquefied only by great pressure at a very low temperature.

It differs in nearly every respect from the other oxide of carbon, CO₂.

Exp. 55. Arrange a flask as for generating hydrogen, and charge it with small pieces of marble. Add dilute hydrochloric acid by means of the funnel tube.

Carbon dioxide is liberated by the action of this on the marble. CaCO_3 , and may be collected in bottles over water, or by downward displacement, as it is heavier than air. Fill several bottles. See Fig. 15.

Exp. 56. Test the contents of a bottle by applying a lighted match. When this is immersed in the gas it is extinguished.

A little lime water poured in the bottle produces a white precipitate.

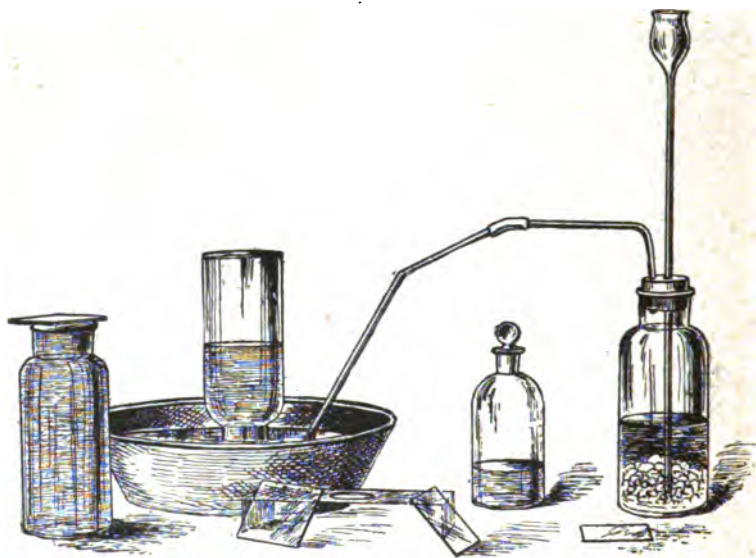


FIG. 15.

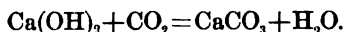
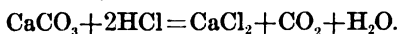
Exp. 57. Extinguish the flame of a match or small candle by pouring the gas on it.

Exp. 58. Bend a glass tube in the form of a siphon. Place the shorter limb in a bottle of the gas, start its flow by aspirating a second or two on the longer limb, and prove that the CO_2 passes through by any of the above tests.

Exp. 59. Pour a few C.c. of lime water in a clean bottle, and from a generator pass in a few bubbles of CO_2 . These at first produce a precipitate; but this disappears after more of the gas has been passed.

This is explained by the fact that the precipitate of calcium carbonate is soluble in water containing carbonic acid.

The reactions occurring in the above experiments are these:



Carbon dioxide is used in large quantities in so-called *soda water*, and other effervescing drinks. It can be made on the large scale by

the above reaction, but must be washed thoroughly by passing through water before it can be used for charging cylinders.

Many of the small fire extinguishers contain water highly charged with carbon dioxide, or chemicals which can be brought together by a simple mechanical device so as to liberate this gas, which, as shown above, readily smothers a fire when present in sufficient quantity.

CARBON AND HYDROGEN.

Although hundreds of compounds are known containing only these elements—the *hydro-carbons* of organic chemistry—but a few will be here mentioned for illustration.

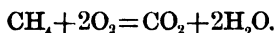
One of the simplest of these is methane, CH_4 , commonly called *marsh gas*.

Exp. 60. Use the apparatus described in experiment 51. Charge it, to about half its capacity, with a dry mixture of one part of sodium acetate and four parts of soda-lime, which should be prepared beforehand and kept for the purpose, and heat gently until gas is evolved. This is collected in bottles and tested by burning. A blue flame results.

The sodium acetate decomposes in the above experiment in this way:



The calcium oxide present in the soda-lime keeps the mass from becoming hard in the tube. On burning, the gas CO_2 and H_2O are formed:



Methane is an important constituent of illuminating gas.

Another hydro-carbon, likewise present in illuminating gas and in the gases escaping from oil wells, is ethylene, C_2H_4 . This is best made as follows:

Exp. 61. Twenty-five Gm. of alcohol and one hundred and fifty Gm. of sulphuric acid are mixed, and heated in a large flask furnished with a funnel tube and connected with two wash-bottles, as in the experiment for making hydrochloric acid. The first wash-bottle contains sulphuric acid, the second caustic soda solution. (See Fig. 7.)

The heat must be gentle at first, and the evolution of the gas should not be allowed to become violent. After it has commenced, a mixture of equal volumes of alcohol and sulphuric acid can be added through the funnel tube. The ethylene, being but slightly soluble, passes through the two wash-bottles, and can be collected over water in the usual way. Test the gas by burning; a large luminous flame is produced.

A few per cent. of this and related gases impart the illuminating power to ordinary coal gas. Petroleum and other mineral oils consist almost entirely of hydro-carbons.

CARBON, OXYGEN AND HYDROGEN.

Many bodies containing these three elements are known, as the acids, alcohols and carbo-hydrates of organic chemistry.

The preparation of a few of them will be given here.

Starch, $C_6H_{10}O_5$, is a product of the growth of plants. From it glucose or *grape sugar* can be made, as here illustrated.

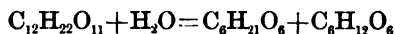
Exp. 62. Rub 10 Gm. of starch to a thin cream with a little water, then add 200 cubic centimeters more and 5 cubic centimeters of dilute sulphuric acid. Boil the mixture in a flask or beaker for several hours, replacing the water lost by evaporation. The starch becomes gradually converted into sugar, while the acid remains unchanged. This must next be removed, which is accomplished by adding powdered chalk as long as there is effervescence. The acid is converted into insoluble calcium sulphate, which is filtered off. The clear filtrate, on evaporation, leaves a residue of glucose, $C_6H_{12}O_6$.

On a large scale the conversion of starch into glucose is accomplished by heating with the small amount of acid under steam pressure.

Exp. 63. Test the glucose made by dissolving it in water and boiling a few drops of this solution with some *Fehling* solution, the preparation of which will be given later, under the head of Volumetric Analysis. This solution contains a hydrate of copper which is "reduced" by the glucose to bright red suboxide of copper, and the appearance of this red precipitate proves the presence (in this case) of the *grape sugar*.

Cane-sugar, or saccharose, $C_{12}H_{22}O_{11}$, cannot be made by such a simple artificial process. It can readily be converted into glucose, however, by heating its solution with a little dilute acid.

Exp. 64. Dissolve about a Gm. of pure crystallized cane-sugar in ten cubic centimeters of water, and divide the solution into two parts. Test the first with the *Fehling* solution. No precipitate is formed. Now boil the second part with two drops of dilute sulphuric acid, for three or four minutes, neutralize with sodium carbonate solution, and test by boiling with the copper solution as before. A red precipitate is formed. Along with the glucose a similar sugar, known as *lævulose*, is formed.



Practically, in the manufacture of fermented liquors starch is converted into maltose, a body somewhat allied to glucose, by means of malt (acid is seldom used), and the sugar solution so obtained is fermented by the addition of yeast. The cells of this little plant can act on the sugar, and break it up into alcohol and carbon dioxide, as in this equation:



Exp. 65. Mix 100 Gm. of glucose syrup or molasses with 500 cubic centimeters of water, and with this solution nearly fill a flask or bottle. A few cubic centimeters of brewer's yeast are added to the contents of the bottle and shaken. The whole apparatus, closed by a cork, through which passes a bent delivery tube, is left at rest, in a moderately warm place, for two or three days. The delivery tube leads into a dry gas bottle, loosely covered.

When the evolution of gas has nearly or quite ceased the stopper can be removed from the bottle. The liquid is to be divided into two parts. The first is to be treated as in Exp. 67, and the other as in Exp. 68.

Exp. 66. Pour some *lime water* in the gas bottle. The formation of a white precipitate shows the presence of CO_2 .

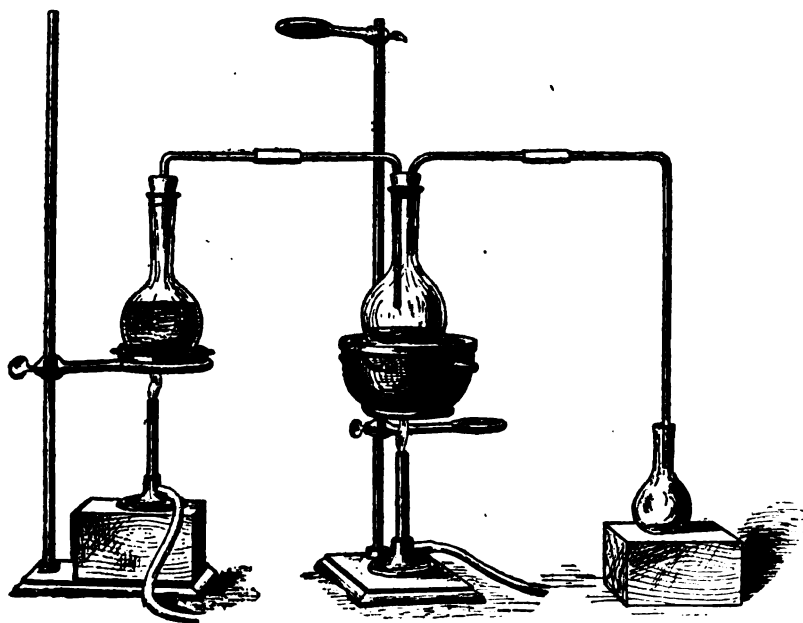


FIG. 16.

Exp. 67. The fermented liquid obtained above contains alcohol, but very largely diluted. It can be separated and tested as follows: Arrange the apparatus as shown in the figure. The first flask, holding about 300 cubic centimeters, contains the liquid, and is heated by a lamp directly. The second flask is kept at a lower temperature by heating it on a water-bath. The delivery tube passes into a small beaker or flask kept cool. (See Fig. 16.)

Alcohol and some water distil from the first flask, while from the second the alcohol with much less water is obtained. This is possible, as the alcohol boils about 20 degrees lower than the water.

The odor of the liquid collected in the small beaker is characteristic. It can also be tested by burning. In practice alcohol can be made of about 93 per cent. strength, by weight. Absolute alcohol is made from the commercial article by removing the remaining water by heating with good freshly burned lime, and distilling over this.

As alcohol is made from sugar by a process of fermentation, so from alcohol, vinegar or acetic acid can be made by an analogous process.

Exp. 68. Allow the second part of the alcoholic liquid to stand for several days in a loosely covered bottle. The acetic acid ferment. present in the air, acts on it gradually in such a manner as to carry oxygen to the alcohol and break it up into the acid and water. The contents of the bottle become sour, and if after standing some days a little powdered chalk is added, a lively effervescence proves the presence of an acid strong enough to liberate CO_2 .

Alcohol can be converted into acetic acid by several other methods. Nearly all strong oxidizing agents are capable of bringing about this reaction.

Practically, large quantities are made from *pyroligneous acid*, the acid liquid obtained in the destructive distillation of wood.

Numerous other examples of combinations of carbon could be given, but these are perhaps sufficient for the present purpose.

The whole subject of organic chemistry is concerned with the study of these multiform combinations.

THE METALS.

CHAPTER V.

SODIUM.

SODIUM.

[NATRIUM.]

Na. 23.

Sp. gr. 0.970.

Sodium is not found free, but in several natural compounds, of which the chloride (salt), and the nitrate (Chili saltpeter), are the most abundant.

It is a soft, white metal, resembling potassium, and is prepared, like this, by reduction of the carbonate by carbon. It decomposes water, and is kept under naphtha.

The compounds are soluble in water, with a few exceptions, and may be recognized by these tests:

1°. Sodium compounds, even in minute traces, color the clear flame of the Bunsen burner intensely yellow.

2°. A fresh solution of potassium pyroantimonate added to a concentrated neutral solution of a sodium salt, produces a white crystalline precipitate of sodium pyroantimonate, $\text{Na}_3\text{H}_2\text{Sb}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$, which separates rather slowly.

This reaction is characteristic of sodium only when other salts, excepting those of potassium, are absent.

Salt serves as the starting-point for most sodium compounds. The sulphate, carbonate and bicarbonate are made in turn from this. The last two are used in making many others.

PREPARATIONS OF SODIUM.

	Formula.	Molecular Weight.	Per cent. of Sodium.
Hydrate	NaOH	40	57.50
Hydrate (solution)	5% NaOH		2.87
Chloride	NaCl	58.4	39.38
Bromide	NaBr	102.8	23.37
Iodide	NaI	149.6	15.38
Sulphite	$\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	252	18.25
Bisulphite	NaHSO_3	104	22.11
Thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	248	18.55
Sulphate	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	322	14.29
Carbonate (cryst.)	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	286	16.08
Carbonate (anhyd.)	Na_2CO_3	106	43.40
Bicarbonate	NaHCO_3	84	27.38
Nitrate	NaNO_3	85	27.06
Phosphate (ord.)	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	358	12.85
Pyrophosphate	$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	446	20.83
Hypophosphite	$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	106	21.70
Chlorate	NaClO_3	106.4	21.62
Bromate	NaBrO_3	150.8	15.25
Iodate	NaIO_3	197.6	11.64
Borate	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	382	12.04
Silicate	Na_2SiO_3	122	37.70
Arsenate (acid)	$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$	312	14.74
Arsenite	Na_2HASO_3	170	27.06
Acetate	$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$	136	16.91
Benzoate	$\text{NaC}_6\text{H}_5\text{O}_2 \cdot \text{H}_2\text{O}$	162	14.20
Carbolate	$\text{NaC}_6\text{H}_7\text{O}$	116	19.83
Citrate	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	294	23.47
Formate	$\text{NaCHO}_2 \cdot \text{H}_2\text{O}$	86	26.74
Oleate	$\text{NaC}_{15}\text{H}_{31}\text{O}_2$	304	7.56
Oxalate	$\text{Na}_2\text{C}_2\text{O}_4$	134	34.33
Salicylate	$2(\text{NaC}_7\text{H}_5\text{O}_3) \cdot \text{H}_2\text{O}$	338	13.61
Santoninate	$2(\text{NaC}_{15}\text{H}_{19}\text{O}_3) \cdot 7\text{H}_2\text{O}$	698	6.59
Sulphocarbolate	$\text{NaC}_6\text{H}_5\text{SO}_3 \cdot 2\text{H}_2\text{O}$	232	9.91
Sulphovinate	$\text{NaC}_6\text{H}_5\text{SO}_4 \cdot \text{H}_2\text{O}$	166	13.85
Tartrate	$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$	230	20.00
Valerate	$\text{NaC}_5\text{H}_9\text{O}_2$	124	18.55

POTASSIUM.

POTASSIUM.

[KALIUM.]

K. 39.

Sp. gr. 0.865.

Potassium does not occur free, but widely distributed in several compounds.

The silvery white metal is reduced by heating a mixture of powdered coal and the carbonate in an iron retort. It decomposes water at ordinary temperature, and must be kept under naphtha.

Most of the compounds are soluble in water, and can be recognized by these tests:

1°. Potassium salts, moistened with sulphuric or hydrochloric acid, impart a blue violet color to the flame of a Bunsen burner, when introduced in the solid form, or best, as strong solution on a platinum wire.

The color is not obscured when viewed through glass colored blue by cobalt.

2°. By adding solution of platinum chloride to a solution of a potassium salt containing a little hydrochloric acid, and then evaporating to dryness on a water-bath, a precipitate of potassium platinum chloride, K_2PtCl_6 , is formed. By pouring water on the residue, everything is dissolved but the K_2PtCl_6 , which is left in the form of fine yellow crystals.

PREPARATIONS OF POTASSIUM.

	Formula.	Molecular Weight.	Per ct. of Potassium
Hydrate	KOH	56	69.64
Hydrate (solution)	5% KOH	—	3.48
Chloride	KCl	74.4	52.44
Bromide	KBr	118.8	32.83
Iodide	KI	165.6	23.55
Cyanide	KCy	65	60
Ferrocyanide	$K_4FeCy_6 \cdot 8H_2O$	422	36.97
Ferricyanide	$K_3Fe_2Cy_{12}$	648	30.11
Sulphide	K_2S_2	174	44.83
Sulphite	$K_2SO_3 \cdot 2H_2O$	194	40.21
Bisulphite	$KHSO_3$	120	32.50
Sulphate	K_2SO_4	174	44.83
Bisulphate	$KHSO_4$	186	28.68
Carbonate	K_2CO_3	188	58.52
Bicarbonate	$KHCO_3$	100	39
Nitrite	KNO_2	85	45.89
Nitrate	KNO_3	101	38.61
Chlorate	$KClO_3$	122.4	31.86
Bromate	$KBrO_3$	166.8	23.38
Iodate	KIO_3	213.6	18.26
Sulphocyanate	$KSCy$	97	40.21
Hypophosphite	KH_2PO_2	104	37.50
Phosphate (acid)	KH_2PO_4	186	28.68
Chromate	K_2CrO_4	194	40.21
Bichromate	$K_2Cr_2O_7$	294	26.53
Permanganate	$KMnO_4$	313.8	24.85
Antimonate	$KSbO_3$	207	18.84
Arsenite	K_3HASO_3	202	38.61
Silicate	K_2SiO_3	154	50.65
Acetate	$KC_2H_3O_2$	98	39.79
Citrate	$K_3C_6H_5O_7 \cdot H_2O$	324	36.11
Oxalate	$K_2C_2O_4 \cdot H_2O$	184	42.39
Oleate	$KC_{18}H_{33}O_2$	320	12.19
Salicylate	$2(KC_7H_5O_3) \cdot H_2O$	370	21.08
Sulphocarbolate	$KC_4H_5SO_4$	212	18.40
Tartrate	$K_2C_4H_4O_6$	226	34.51
Bitartrate	$KHC_4H_4O_6$	188	20.74
— sodium tartrate	$KNaC_4H_4O_6 \cdot 4H_2O$	282	13.83

A large number of potassium compounds are used in pharmacy and in the general arts. Native potassium chloride, found in large quantities near Stassfurt, Germany, is the source from which most of them are prepared indirectly. This is converted into the sulphate and the sulphate into the carbonate, from which the bicarbonate can be obtained in pure condition. The hydrate can also be prepared from the carbonate, and serves, like the bicarbonate, for the preparation of many compounds.

Formerly, the carbonate was made by leaching wood ashes and evaporating. This gave a crude "pot-ash" from which the pure K_2CO_3 was obtained. It was made, also, by calcining "cream of tartar," potassium bitartrate, deposited as "argols" in the fermentation of wine.

LITHIUM.

LITHIUM.

Li. 7.

Sp. gr. 0.59.

Lithium is a rare metal found in several minerals, and in minute quantity in the waters of certain springs.

The metal is silvery white, and is reduced from the fused chloride by electricity. It oxidizes in moist air, and decomposes water. The salts are generally colorless, and mostly soluble in water. They may be recognized by these tests:

1°. Lithium salts impart an intense crimson red color to the clear flame of the Bunsen burner.

2°. Solution of sodium phosphate boiled with solution of a lithium salt produces a crystalline precipitate of lithium phosphate, $2Li_3PO_4 \cdot H_2O$.

From its low atomic weight, lithium has a great saturating power, 7 parts being equivalent to 23 of sodium or 39 of potassium.

The carbonate is the most important compound, and is used in the preparation of the others.

PREPARATIONS OF LITHIUM.

	Formula.	Molecular Weight.	Per ct. of Lithium.
Oxide	Li_2O	30	46.66
Hydrate	$LiOH$	24	29.17
Chloride	$LiCl$	42.4	16.51
Bromide	$LiBr$	86.8	8.06
Iodide	LiI	133.6	5.24
Carbonate	Li_2CO_3	74	18.92
Benzoate	$LiC_6H_5O_2$	128	5.47
Citrate	$Li_3C_6H_5O_7$	210	10.00
Salicylate	$2LiC_7H_5O_3 \cdot H_2O$	306	4.58

AMMONIUM.

AMMONIUM.

NH₃, 18.

Sp. gr. —

The free existence of this radical is doubtful, but numerous compounds are known.

In the destructive distillation of coal (manufacture of illuminating gas), most of the nitrogen present combines with hydrogen, oxygen and carbon to form ammonium carbonate, which passes along with the gas until it is intercepted by the water in the *hydraulic main*. This is replaced by fresh water from time to time, and the ammonium carbonate it holds is converted into sulphate or chloride by acid, and recovered by evaporation and distillation.

The following tests are sufficient for the recognition of the ammonium salts:

1°. Boiled with solution of a fixed alkaline hydrate, as KOH or NaOH, ammonium compounds are decomposed. NH₃ is liberated, which can be recognized by its smell or action on red litmus paper.

2°. Solution of platinum chloride, PtCl₄, precipitates from solution of ammonium salts, acidified with hydrochloric acid, crystalline yellow ammonium platinum chloride, (NH₄)₂PtCl₆. Dilute solutions must be concentrated before applying this test.

The general and pharmaceutical uses of ammonium compounds are various. The sulphate and chloride, prepared as before, serve as the material from which the others are made.

PREPARATIONS OF AMMONIUM AND AMMONIA.

	Formula.	Molecular Weight.	Per cent. of NH ₃ .
Ammonia.....	NH ₃	17	100.00
Ammonia, spirit of.....	10NH ₃		10.00
Hydrate.....	NH ₄ OH.....	35	48.57
Hydrate (solution).....	10NH ₃		10.00
Hydrate (solution).....	28NH ₃		28.00
Chloride.....	NH ₄ Cl.....	53.4	31.83
Bromide.....	NH ₄ Br.....	97.8	17.39
Iodide.....	NH ₄ I.....	144.6	11.76
Sulphide.....	(NH ₄) ₂ S.....	68	50.00
Sulphate.....	(NH ₄) ₂ SO ₄	132	25.76
Nitrate.....	NH ₄ NO ₃	80	21.25
Carbonate (commercial).....	(NH ₄)HCO ₃ ·(NH ₄)(NH ₄)CO ₂	(157)	(21.66)
Phosphate.....	(NH ₄) ₂ HPO ₄	132	25.76
Acetate.....	NH ₄ C ₂ H ₃ O ₂	77	22.08
Acetate (solution).....	15NH ₄ C ₂ H ₃ O ₂		3.31
Benzoate.....	NH ₄ C ₆ H ₅ O ₂	139	12.23
Citrate.....	(NH ₄) ₃ C ₆ H ₅ O ₇	243	20.99
Oxalate.....	(NH ₄) ₂ C ₂ O ₄ ·H ₂ O.....	142	23.94
Tartrate.....	(NH ₄) ₂ C ₄ H ₄ O ₆	184	18.48
Valerate.....	NH ₄ C ₅ H ₉ O ₂	119	14.29

CALCIUM.

CALCIUM.

Ca. 40.

Sp. gr. 1.6.

Calcium does not occur in the free state, but very abundantly in numerous compounds, of which the carbonate (marble, lime-stone, chalk) and sulphate (gypsum) are the most important. Silicates, phosphates and other salts are found in smaller quantity.

The metal is brassy yellow, and can be best prepared by reduction of the fused chloride by means of a strong galvanic current. Most of the salts are soluble in water or dilute acids, and are recognized by these tests.

1°. Alkaline carbonates precipitate white calcium carbonate, CaCO_3 , from solutions of calcium salts.

2°. Ammonium oxalate throws down from neutral or alkaline solutions white calcium oxalate, CaC_2O_4 , aq., insoluble in excess or in acetic acid.

3°. Sulphuric acid and soluble sulphates precipitate calcium sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, from solutions which are not too dilute. From weak solutions the precipitate settles out very slowly; its formation may be hastened by the addition of 2 volumes of alcohol.

4°. Calcium chloride and other compounds moistened with hydrochloric acid impart a yellowish red color to the clear flame of a Bunsen burner. The reaction shows best with the chloride. It is obscured by presence of barium, strontium or sodium compounds.

PREPARATIONS OF CALCIUM.

	Formula.	Molecular Weight.	Per ct. of Calcium.
Oxide	CaO	56	71.43
Hydrate	Ca(OH)_2	74	54.05
Hydrate (solution)	0.15% Ca(OH)_2		.08
Chloride	CaCl_2	110.8	36.10
Bromide	CaBr_2	199.6	20.04
Iodide	CaI_2	298.2	13.64
Sulphide	CaS	72	55.55
Sulphate	CaSO_4	136	29.41
Sulphite	$\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$	156	25.84
Nitrate	$\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$	236	16.94
Carbonate	CaCO_3	100	40.00
Iodate	$\text{Ca(IO}_3)_2 \cdot 6\text{H}_2\text{O}$	497.2	8.06
Phosphate	$\text{Ca}_3(\text{PO}_4)_2$	310	38.71
Phosphate (acid)	$\text{CaH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	252	15.86
Hypophosphite	$\text{CaH}_2(\text{PO}_2)_2$	170	23.53
Hypochlorite	CaO_2Cl_2	142.8	38.01
Oxalate	$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	164	24.89

Calcium carbonate serves as the raw material from which most of the other salts are made. It occurs very pure as marble and calc-spar. An impure form contains magnesium carbonate, and is known as *magnesium lime-stone*.

BARIUM.

BARIUM.

Ba. 137.

Sp. gr. 4+

Barium is found chiefly as carbonate and sulphate.

The pale yellow metal can be obtained, with difficulty, by electrolyzing the fused chloride.

The barium salts, with the exception of the sulphate, dissolve in water or acids. The characteristic tests are:

1°. Alkaline carbonates precipitate barium carbonate, BaCO_3 , readily soluble in dilute acids.

2°. Ammonium oxalate precipitates from neutral or alkaline solutions of barium salts white barium oxalate, $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, which is soluble in oxalic or acetic acid. On standing, however, the barium precipitates from such a solution as binoxalate.

3°. Sulphuric acid or soluble sulphates precipitate solutions of barium compounds as white barium sulphate, BaSO_4 . This is one of the most insoluble of artificial compounds, and is attacked but slightly by boiling concentrated acids.

4°. Potassium bichromate precipitates from neutral or acetic acid solutions of barium salts yellow barium chromate, BaCrO_4 , soluble in dilute hydrochloric and nitric acids.

5°. Barium compounds impart a yellowish green color to the flame of the Bunsen burner. The reaction is obscured by the presence of several other metals.

Barium carbonate is the source from which most of the barium compounds are made. Native barium sulphate is used in paint.

PREPARATIONS OF BARIUM.

	Formula.	Molecular Weight.	Per cent of Barium.
Oxide	BaO	153	89.54
Oxide (per)	BaO_2	169	81.07
Hydrate	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	315	48.49
Chloride	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	248.8	56.19
Sulphide	BaS	169	81.07
Sulphate	BaSO_4	233	58.80
Nitrate	$\text{Ba}(\text{NO}_3)_2$	261	52.49
Carbonate	BaCO_3	197	69.54

STRONTIUM.**STRONTIUM.**

Sr. 87.4.

Sp. gr. 2.5.

'Strontium is found as carbonate and sulphate.' The metal can be reduced by electrolysis of the fused chloride, and so prepared it is yellow and malleable.

In combination it may be recognized by these tests:

1°. Alkaline carbonates precipitate strontium carbonate, SrCO_3 , soluble in acetic and dilute nitric and hydrochloric acids.

2°. Soluble sulphates or sulphuric acid precipitate white strontium sulphate, SrSO_4 , which settles out from dilute solutions rather slowly. A dilute solution of potassium sulphate (1—200) will precipitate SrSO_4 on standing. (Difference from Ca.)

3°. Potassium bichromate solution does not precipitate solutions of strontium compounds.

4°. Strontium chloride, and other compounds moistened with hydrochloric acid, impart a deep red color to the flame of the Bunsen burner. The nitrate and chloride of strontium are used in fireworks.

PREPARATIONS OF STRONTIUM.

	Formula.	Molecular Weight.	Per cent. of Strontium.
Oxide.....	SrO	103.4	84.52
Hydrate.....	$\text{Sr(OH)}_2 \cdot 8\text{H}_2\text{O}$	265.4	32.93
Chloride.....	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	266.2	32.83
Sulphate.....	SrSO_4	183.4	47.66
Nitrate.....	$\text{Sr(NO}_3)_2$	211.4	41.34
Carbonate.....	SrCO_3	147.4	59.29
Chlorate.....	$\text{Sr(ClO}_3)_2$	254.2	34.38

MAGNESIUM.**MAGNESIUM.**

Mg. 24.

Sp. gr. 1.74.

Magnesium occurs as carbonate and silicate among rocks, and in sea and spring water as sulphate, bromide and chloride. The metal is best obtained by fusing the chloride with sodium. It is soluble in acids, and, when not quite pure, in water, forming hydrate.

The analytical characteristics of the compounds are:

1°. Potassium and sodium carbonates precipitate basic magnesium carbonate, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, readily soluble in dilute acids and in ammonium chloride solution.

2°. Ammonium carbonate, in absence of other ammonium salts, precipitates white magnesium carbonate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$.

This precipitate is readily soluble in excess of ammonium chloride (difference from Ca, Ba and Sr).

3°. Ordinary sodium phosphate, HNa_2PO_4 , precipitates from solutions containing ammonium hydrate and ammonium chloride, white crystalline ammonium magnesium phosphate, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$. This is readily soluble in dilute acid.

4°. Magnesium compounds impart no color to the flame of a Bunsen burner.

Magnesium is largely used for the production of an intense white light (by burning) employed in photography, and for signaling at sea.

Many of the salts are of pharmaceutical importance, and are obtained from the basic carbonate or sulphate.

PREPARATIONS OF MAGNESIUM.

	Formula.	Molecular Weight.	Per cent. of Magnesium
Oxide	MgO	40	60.00
Hydrate	$\text{Mg}(\text{OH})_2$	58	41.88
Chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	202.8	11.83
Bromide	$\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$	291.6	8.23
Iodide	MgI_2	277.2	8.66
Sulphate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	246	9.75
Sulphite	$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$	212	11.32
Nitrate	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	256	9.38
Carbonate (basic)	$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	502	23.90
Phosphate	$\text{Mg}_3(\text{PO}_4)_2$	262	27.48
Acetate	$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$	142	16.90
Citrate	$\text{MgHC}_6\text{H}_5\text{O}_7$	214	11.21

CHAPTER VI.

ZINC.

ZINCUM.

Zn. 64.9

Sp. gr. 6.8-7.2.

Zinc occurs usually as sulphide or *blende*, ZnS , and as carbonate, or *calamine*, ZnCO_3 . The metal is obtained by roasting the ore to oxide, and then reducing this by means of powdered coal.

It is readily soluble in dilute acids.

The metal may be recognized by its color and other physical properties.

In compounds the following tests serve for identification:

1°. Ammonium, potassium and sodium hydrates precipitate from solutions of zinc salts white zinc hydrate, Zn(OH)_2 , which dissolves in an excess of the precipitant.

2°. Hydrogen sulphide precipitates from alkaline solutions white hydrated sulphide, $\text{ZnS.H}_2\text{O}$. In neutral solutions the precipitation is only partial; strong acids prevent it, but from solutions containing only acetic acid it is complete. The same precipitate is formed by ammonium sulphide. It is insoluble in excess of the precipitant and in alkaline hydrates. It dissolves easily in dilute mineral acids.

3°. Sodium carbonate precipitates basic zinc carbonate, which varies in composition according to the temperature and concentration of the solutions. These precipitates are white and insoluble in an excess of the reagent.

4°. Potassium chromate precipitates from neutral solutions of zinc salts, basic zinc chromate, $\text{ZnCrO}_4 \cdot \text{Zn(OH)}_2$, yellow.

Zinc is used as a covering for iron (galvanized iron), in sheets for various purposes, in brass and other alloys, in galvanic batteries, and in the preparation of several salts. The solution of zinc in dilute hydrochloric or sulphuric acid affords the best means of preparing hydrogen.

PREPARATIONS OF ZINC.

	Formula.	Molecular Weight.	Per cent. of Zinc.
Oxide.....	ZnO	80.9	80.22
Chloride.....	ZnCl_2	135.7	47.83
Chloride (solution).....	50 per cent. ZnCl_2		28.92
Bromide.....	ZnBr_2	224.5	28.91
Iodide.....	ZnI_2	318.1	20.40
Cyanide.....	ZnCy_2	116.9	55.52
Ferrocyanide.....	Zn_2FeCy_6	341.8	37.97
Sulphide.....	ZnS	96.9	66.98
Sulphate.....	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	286.9	22.62
Carbonate (basic).....	$2(\text{ZnCO}_3) \cdot 3\text{Zn(OH)}_2$	546.5	59.38
Phosphide.....	Zn_3P_2	256.7	75.85
Acetate.....	$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	236.9	27.39
Valerate.....	$\text{Zn}(\text{C}_4\text{H}_7\text{O}_2)_2 \cdot \text{H}_2\text{O}$	284.9	22.78
Oleate.....	$\text{Zn}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$	626.9	10.35
Lactate.....	$\text{Zn}(\text{C}_3\text{H}_5\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	296.9	21.86
Sulpho-carbolate.....	$\text{Zn}(\text{C}_6\text{H}_5\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$	554.9	11.69
Salicylate.....	$\text{Zn}(\text{C}_7\text{H}_5\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	392.9	16.52

COBALT.

COBALTUM.

Co. 59.

Sp. gr. 8.9.

Cobalt occurs usually associated with nickel compounds. The reduction of the metal is an expensive operation. It resembles nickel in most of its properties.

The hydrated salts are red and the anhydrous salts blue, as a rule.

The chief tests are these:

1°. Hydrogen sulphide does not precipitate acid solutions of cobalt salts.

2°. Ammonium sulphide precipitates black cobalt sulphide, CoS , from solutions of cobalt compounds. It is insoluble in excess of the reagent and in dilute acids.

3°. Potassium and sodium hydrates precipitate from hot solutions red cobalt hydrate, Co(OH)_2 , which soon turns dark brown from absorption of oxygen. From cold solutions a bluish basic precipitate is thrown down, insoluble in excess.

4°. Ammonium hydrate throws down from neutral solutions, free from ammonium salts, basic hydrates, which dissolve readily in excess. In presence of ammonium salts very peculiar complicated compounds are formed without precipitation.

5°. From a cobalt solution containing an excess of acetic acid, potassium nitrite precipitates the metal completely in the form of a lemon yellow crystalline compound containing nitrites of cobalt and potassium, $\text{Co}_2(\text{NO}_2)_6 + 6\text{KNO}_2 + \text{water}$.

The amount of water depends on the concentration of the solutions.

This precipitate is characteristic, and distinguishes cobalt from nickel.

6°. Cobalt compounds impart a deep blue color to the borax bead. A mere trace is sufficient to show this reaction.

An impure silicate of cobalt known as *smalt*, is used to impart a deep blue color to glass or pottery.

A solution of cobalt chloride is employed as a sympathetic ink. This appears almost colorless on paper, but becomes blue on application of heat.

PREPARATIONS OF COBALT.

	Formula.	Molecular Weight.	Per cent. of Cobalt.
Oxide (ous).....	CoO	75	78.66
Oxide (ic).....	Co_2O_3	166	71.08
Chloride.....	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	287.8	24.81
Bromide.....	$\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$	326.6	18.07
Iodide.....	$\text{CoI}_2 \cdot 6\text{H}_2\text{O}$	420.2	14.04
Cyanide.....	CoCy_2	111	53.15
Sulphide.....	CoS	91	64.83
Sulphate.....	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	281	20.98
Nitrate.....	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	291	20.28
Carbonate.....	$\text{CoCO}_3 \cdot 6\text{H}_2\text{O}$	227	25.99

NICKEL.

NICCOLUM.

Ni. 58.

Sp. gr. 8.9.

Nickel occurs native in meteoric iron. Found usually combined with arsenic, antimony, or sulphur, and associated with other ores. The process of extracting the metal is complex.

It is silvery white, takes a good polish, does not tarnish readily and dissolves in dilute mineral acids. Its salts containing water of crystallization are usually green; anhydrous they are yellow. The following are the chief analytical tests:

1°. Hydrogen sulphide does not precipitate acid solutions of nickel salts.

2°. Ammonium sulphide produces in solutions of nickel salts a black precipitate of nickel sulphide, NiS , which is slightly soluble in

excess. The precipitate is practically insoluble in cold dilute hydrochloric acid and in acetic acid, but dissolves in *aqua regia*.

3°. Ammonium hydrate produces in solutions of nickel salts a light green precipitate, which disappears on addition of an excess, giving a blue liquid containing a double compound of nickel and ammonium.

4°. Potassium and sodium hydrates precipitate from solutions of nickel salts greenish nickel hydrate, $\text{Ni}(\text{OH})_2$, which is not soluble in excess.

5°. Potassium cyanide precipitates nickel cyanide, NiCy_2 , from solutions, and redissolves it when added in excess, forming a dark yellow solution. If this is treated with an excess of sodium hypochlorite solution and boiled, the nickel precipitates as black hydrated peroxide, $\text{Ni}_2(\text{OH})_6$.

6°. Compounds of nickel fused in the borax bead impart to it a reddish brown color, visible on cooling.

Nickel is chiefly used for plating, and as an alloy in coins and instruments of various kinds. The salts are best prepared from the carbonate or oxide.

PREPARATIONS OF NICKEL.

	Formula.	Molecular Weight.	Per cent. of Nickel.
Oxide (ous)	NiO	74	78.88
Oxide (ic)	Ni_2O_3	164	70.72
Chloride	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	236.8	24.49
Bromide	$\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$	271.6	21.85
Iodide	$\text{NiI}_2 \cdot 6\text{H}_2\text{O}$	419.2	18.84
Cyanide	NiCy_2	110	52.78
Sulphide	NiS	90	64.44
Sulphate	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	280	20.71
— ammon. sulphate	$\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	394	14.72
Nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	290	20.00
Carbonate	$\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$	226	25.66

MANGANESE.

MANGANUM.

Mn. 53.9.

Sp. gr. 7.99.

Manganese is not found native, but usually as black oxide, or *pyrolusite*, MnO_2 .

The metal can be obtained by reduction of one of the artificial oxides by charcoal at a high temperature. It has no practical uses. The compounds can be recognized by these tests:

1°. Manganese compounds fused with dry sodium carbonate and a little potassium nitrate on a platinum foil yield sodium manganate,

Na_2MnO_4 , green while hot, and bluish green on cooling. This is a delicate and characteristic test.

2°. Ammonium sulphide produces in neutral or alkaline solutions of manganese salts a light colored precipitate of manganous sulphide, $\text{MnS} \cdot \text{H}_2\text{O}$. This turns brown on standing in the air, and is readily soluble in dilute acids.

3°. Potassium, sodium or ammonium hydrate produces in solutions of manganese salts a dirty white precipitate of manganous hydrate, $\text{Mn}(\text{OH})_2$. Exposed to the air, this absorbs oxygen and turns dark brown from the formation of manganic hydrate. The manganous hydrate redissolves in a solution containing an excess of ammonium chloride, but the brown hydrate, produced by exposure to the air, does not.

4°. Manganates or permanganates would not be recognized by the above precipitation tests. Solutions of the first are green; of the second, purple. In the ordinary course of analysis these would become reduced, leaving the manganese in the form of a salt, suitable for precipitation.

The black oxide of manganese is the source from which all manganese compounds are obtained, directly or indirectly.

This oxide is used in large quantities for the manufacture of chlorine gas by decomposition of hydrochloric acid.

PREPARATIONS OF MANGANESE.

	Formula.	Molecular Weight.	Per cent. of Manganese.
Oxide (ous)	MnO	69.9	77.11
Oxide (ic)	Mn_2O_3	155.8	69.19
Oxide (hyper)	MnO_2	85.9	62.75
Chloride	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	196.3	27.46
Iodide	MnI_2	307.1	17.55
Bromide	$\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$	285.5	18.88
Sulphate	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	221.9	24.29
Carbonate	MnCO_3	118.9	47.32
Nitrate	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	285.9	18.85
Phosphate	$\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$	477.7	33.85
Tannate			
Tartrate	$\text{MnC}_4\text{H}_4\text{O}_6$	201.9	26.60
Potass. permanganate	$\text{K}_2\text{Mn}_2\text{O}_8$	313.8	34.35

URANIUM.

URANIUM.

U. 239.5

Sp. gr. 18.7.

Uranium is a rare metal, found as an oxide, *pitchblende*, and as a phosphate. Two classes of salts are known: uranous and uranic. The former are green and the latter yellow.

The uranic salts are recognized as follows:

1°. Ammonium carbonate produces a yellow precipitate, which dissolves in excess.

2°. Solution of potassium ferrocyanide produces a reddish brown precipitate, even in very dilute solutions.

PREPARATIONS OF URANIUM.

	Formula.	Molecular Weight.	Per cent. of Uranium.
Oxide	UO_2	287.5	83.30
Nitrate	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	508.5	47.56
Acetate	$\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 5\text{H}_2\text{O}$	425.5	56.29

IRON.

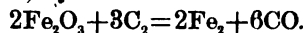
FERRUM.

Fe. 56.

Sp. gr. 7.8.

Iron has been found native, but it usually occurs as oxides, carbonate or sulphide.

The metal is reduced in the blast furnace, from the oxides (or carbonate after calcination) by some form of carbon.



Exp. 69. An experiment showing the reduction of iron by hydrogen is performed in this way: Prepare a tube of hard glass, 15 to 20 Cm. long and $1\frac{1}{4}$ Cm. in internal diameter. By means of perforated corks attach smaller tubes to each end. One of them is connected with a hydrogen generator, and the other is drawn out so as to leave a coarse point. Precipitate some ferric hydrate, by the action of ammonium hydrate on solution of ferric chloride, wash and dry it thoroughly, and powder the resulting peroxide. Introduce several Gm. of this into the glass tube, pass a current of gas from the generator, and by means of a Bunsen burner heat the tube, gradually at first, but finally very strongly. (See Fig. 17.)

The hydrogen combines with the oxygen of the oxide, forming water, which escapes as steam, while a grayish black powder of reduced

iron remains in the tube. This is the *ferrum reductum* of the Pharmacopœia.

Iron dissolves readily in hydrochloric, sulphuric, and cold dilute nitric acid, producing ferrous salts; in strong nitric acid ferric nitrate is formed. The chief tests are these:

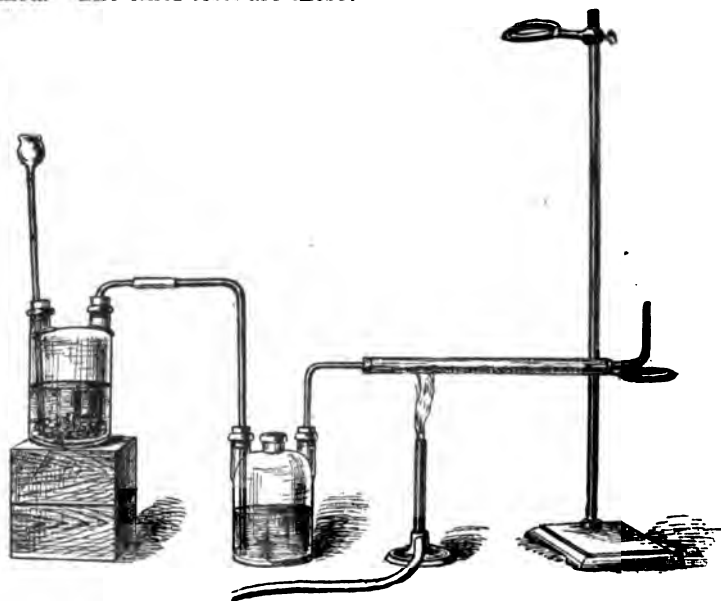


FIG. 17.

1°. Hydrogen sulphide does not precipitate neutral or acid solutions of iron compounds, but alkaline solutions are thrown down as black ferrous sulphide, FeS . In case of ferric compounds this precipitation is attended by separation of sulphur. The precipitate is readily soluble in dilute acids.

2°. Ammonium sulphide precipitates ferrous sulphide from solutions of ferrous salts, and ferrous sulphide + sulphur from solutions of ferric salts.

3°. Ammonium hydrate added in excess to solutions of ferric salts produces a red precipitate of ferric hydrate, $\text{Fe}_2(\text{OH})_6$. From solutions of ferrous salts containing no other ammonium compounds a dirty white precipitate of ferrous hydrate, $\text{Fe}(\text{OH})_2$, is thrown down. This finally becomes red by oxidation in contact with the air. If ammonium salts are present in sufficient quantity no precipitate is formed at first by action of ammonium hydrate.

4°. Potassium sulphocyanate produces in solutions of ferric salts, but not in solutions of ferrous salts free from ferric, deep red soluble ferric sulphocyanate, $\text{Fe}_2\text{S}_2\text{Cy}_6$. This is a very delicate and character-

istic reaction. In presence of several organic salts the color appears only after the addition of hydrochloric acid. A similar color is given by nitric acid containing nitrous, but in this case it disappears on warming with alcohol.

5°. Potassium ferricyanide does not precipitate ferric solutions, but in ferrous solutions it produces deep blue ferrous ferricyanide, $\text{Fe}_3\text{Fe}_2\text{Cy}_{12}$. In very weak solutions only a greenish blue color is produced.

6°. Potassium ferrocyanide produces in solutions of ferric salts deep blue *Prussian blue*, ferric ferrocyanide, $\text{Fe}_4\text{Fe}_3\text{Cy}_{12}$. This reaction is likewise very delicate. Ferrous solutions give with this reagent a bluish white precipitate which gradually becomes deeper colored by absorption of oxygen from the air.

PREPARATIONS OF IRON.

	Formula.	Molecular Weight.	Per cent. of Iron.
Oxide (ous).....	FeO	72	77.77
Oxide (ous, ic).....	Fe_3O_4	232	72.41
Oxide (ic).....	Fe_2O_3	160	70.00
Hydrate.....	$\text{Fe}_2(\text{OH})_2$	214	52.33
Chloride (ous).....	FeCl_2	126.8	44.16
Chloride (ic).....	Fe_2Cl_6	324.4	84.52
Bromide (ous).....	FeBr_2	215.6	25.97
Bromide (ic).....	Fe_2Br_6	590.8	18.95
Iodide.....	FeI_2	309.2	18.11
Sulphide (ous).....	FeS	88	63.63
Sulphide (ic).....	FeS_2	120	46.66
Sulphate (ous).....	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	20.14
Sulphate (ic).....	$\text{Fe}_2(\text{SO}_4)_3$	400	28.00
— ammon. sulph. (ous).....	$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	392	14.28
— ammon. sulph. (ic).....	$\text{Fe}_2(\text{NH}_4)_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$	964	11.61
Nitrate.....	$\text{Fe}_2(\text{NO}_3)_6 \cdot 12\text{H}_2\text{O}$	700	16.00
Carbonate.....	FeCO_3	116	48.27
Hypophosphite.....	$\text{Fe}_2(\text{H}_2\text{PO}_2)_2$	502	22.31
Phosphate (ous).....	$\text{Fe}_2(\text{PO}_3)_2 \cdot 8\text{H}_2\text{O}$	502	33.46
Phosphate (ic).....	$\text{Fe}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	374	29.94
Pyrophosphate.....	$\text{Fe}_2(\text{P}_2\text{O}_7)_2$	746	30.02
Ferrocyanide (ic).....	$\text{Fe}_4(\text{FeCy}_6)_3$	860	45.58
Ferricyanide (ous).....	$\text{Fe}_3(\text{Fe}_2\text{Cy}_{12})$	592	47.29
Arsenate (basic).....	$\text{Fe}_3\text{O}_5(\text{AsO}_4)_2 \cdot 16\text{H}_2\text{O}$	1089	30.83
Acetate.....	$\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$	174	32.18
Citrate.....	$\text{Fe}_2(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$	598	18.72
— ammon. citrate.....			
— quinine citrate.....			
— strychnine citrate.....			
Lactate.....	$\text{Fe}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 8\text{H}_2\text{O}$	288	19.44
Oxalate.....	$\text{FeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	162	34.57
Tartrate.....	$\text{FeC}_4\text{H}_4\text{O}_6$	204	27.45
— ammon. tartrate.....			
— potass. tartrate.....			
Valerate.....	$\text{Fe}_2(\text{C}_5\text{H}_9\text{O}_2)_2$	718	15.59

The ordinary uses of iron are well known. In the laboratory it is employed in stands, tongs, furnaces, oil and sand-baths, etc., on account of its strength and relative cheapness. For several of these purposes brass

would be preferable, as iron oxidizes very readily in the air of a laboratory. In the form of wrought iron it is used in pipes for conveying water, and in stills and boilers for operations on a large scale.

In the form of fine wire it is used in the direct preparation of several pharmaceutical products.

ALUMINIUM.

ALUMINIUM.

Al. 27.

Sp. gr. 2.67.

Aluminium occurs chiefly as silicate in clay and various minerals. Occurs also in alum shales, from the disintegration of which it is obtained as sulphate.

The reduction of the metal is somewhat expensive, as it is accomplished by the action of sodium on the double chloride of aluminium and sodium, itself an artificial product.

The metal is recognized by its light color and low specific gravity. Solutions of potassium and sodium hydrates and hydrochloric and sulphuric acids dissolve it. Nitric acid does not.

The artificial compounds are soluble in water or acids, and are recognized by these tests:

1°. Ammonium hydrate precipitates gelatinous aluminium hydrate, $\text{Al}_2(\text{OH})_6$, which is very slightly soluble in an excess of the reagent.

2°. Potassium and sodium hydrates produce the same precipitate, but in excess redissolve it completely. If ammonium chloride is added to such a solution, which is then warmed, the whole of the $\text{Al}_2(\text{OH})_6$ reprecipitates.

3°. Barium carbonate in finely divided condition, digested with solutions of aluminium salts, produces in the latter a precipitate of basic aluminium hydrate.

The acid of the salt combines with the barium, while CO_2 is liberated.

Presence of organic matters, as sugar, tartaric acid, and citric acid, interferes with the above tests. When present they should be removed by ignition.

4°. If an aluminium compound is strongly heated on charcoal with the blow-pipe, then moistened with solution of cobalt nitrate and again ignited, a deep blue color is produced, which shows best on cooling. This color is due to the formation of a complex compound containing cobalt and aluminium, but is not an absolutely certain test for the latter, as a few other substances give the same reaction.

Metallic aluminium is used in the manufacture of several instruments and in weights. Also in several alloys, as *aluminium bronze*. The sulphate serves as the starting-point for making most of the compounds.

PREPARATIONS OF ALUMINIUM.

	Formula.	Molecular Weight.	Per cent. of Aluminium
Oxide	Al_2O_3	102	52.94
Hydrate	$\text{Al}_2(\text{OH})_6$	156	34.61
Chloride	Al_2Cl_6	266.4	20.27
Sulphate	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	666	8.10
— potass. sulph.	$\text{Al}_2\text{K}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$	948	5.69
— potass. sulph.	$\text{Al}_2\text{K}_2(\text{SO}_4)_4$	516	10.46
— ammon. sulph.	$\text{Al}_2(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$	906	5.96
Nitrate	$\text{Al}_2(\text{NO}_3)_6 \cdot 18\text{H}_2\text{O}$	750	7.20
Acetate	$\text{Al}_2(\text{C}_2\text{H}_3\text{O}_2)_6$	408	13.23

CHROMIUM.

CHROMIUM.

Cr. 52.

Sp. gr. 7.3.

Chromium occurs chiefly as chrome ironstone and also as lead chromate.

The metal can be obtained by reducing the chloride by zinc or by electrolysis. It has no commercial importance.

Chromium appears in two classes of compounds, as it may perform either a basic or acid function. Potassium chromate, K_2CrO_4 , may be taken as the type of one class, chromium sulphate, $\text{Cr}_2(\text{SO}_4)_3$, as the type of the other.

Reducing agents convert chromates into salts of chromium, while oxidizing agents fused with the latter convert them into chromates or bichromates.

The following experiments illustrate this:

Exp. 70. Powder 20 Gm. of potassium bichromate, dissolve it in water in a porcelain dish, add 15 to 20 cubic centimeters of strong sulphuric acid, and cool the mixture. Now add about 10 cubic centimeters of alcohol, and stir. Notice the change of color from red to dark violet.

The alcohol acts as the reducing agent, giving up part of its hydrogen, and becoming converted into aldehyde (and acetic acid), as shown by the following equation:



If the solution is allowed to stand a few days, crystals of chrome alum, $K_2Cr_2(SO_4)_3 \cdot 24H_2O$, separate out, and can be obtained by pouring off the mother liquor.

Exp. 71. Now try a second experiment by powdering these or similar crystals and drying this powder by application of heat. Fuse a little of it with a mixture of dry sodium carbonate and potassium chlorate on platinum foil. When cool the fused mass is dissolved in water, forming a deep yellow solution of potassium and sodium chromates. If this is heated with a little acid it turns red, from formation of bichromates.

Chromium is recognized in its compounds by the following tests:

1°. Ammonium hydrate precipitates from solutions of chromium salts greenish chromium hydrate, $Cr_2(OH)_6$, slightly soluble in an excess of the precipitant, but which is thrown down completely on boiling.

2°. Potassium and sodium hydrates produce the same precipitate, under similar circumstances, but redissolve it when in excess. By adding ammonium chloride and boiling, the hydrate comes down again, completely.

3°. Barium carbonate digested with solutions of chromium salts precipitates basic chromium hydrate. Organic matters interfere with the above tests, as in the case of aluminium.

4°. All chromium compounds fused with potassium chlorate and sodium carbonate give the same reaction as described above.

5°. Chromates or bichromates can be recognized by their color, yellow or red, or by dissolving in water, with addition of sulphuric or hydrochloric acid, and then reducing with hydrogen sulphide, sulphurous anhydride or alcohol. The solution so obtained gives the tests by precipitation, described above.

Potassium bichromate is made directly from the chrome iron ore, and serves as the material from which the other compounds are made.

PREPARATIONS OF CHROMIUM.

	Formula.	Molecular Weight.	Per cent. of Chromium.
Oxide (lc)	Cr_2O_3	152	68.42
Oxide (hyper)	CrO_3	100	52.
Chloride	$Cr_2Cl_6 \cdot 12H_2O$	582.4	19.53
Sulphate	$Cr_2(SO_4)_3 \cdot 18H_2O$	716	14.52
— potass. sulph.	$Cr_2K_2(SO_4)_3 \cdot 24H_2O$	998	10.42
Potass. chromate	K_2CrO_4	194	26.80
Potass. bichromate	$K_2Cr_2O_7$	294	35.37
Ammon. chromate	$(NH_4)_2CrO_4$	152	34.21
Ammon. bichromate	$(NH_4)_2Cr_2O_7$	252	41.26
Barium chromate	$BaCrO_4$	253	20.55
Lead chromate	$PbCrO_4$	322.5	16.12
Silver chromate	Ag_2CrO_4	337.4	15.69

CERIUM.**CERIUM.**

Ca. 140.5

Sp. gr. 6.73.

Cerium is a rare metal, in its physical properties somewhat like iron, but with lower melting point.

The following tests are characteristic of cerium salts:

1°. Potassium hydrate produces a white precipitate, insoluble in excess, and which turns yellow on exposure to the air.

2°. Strong solution of potassium sulphate, added in excess, precipitates white cerous potassium sulphate from solutions of cerous salts.

3°. Solution of oxalic acid precipitates white cerous oxalate.

PREPARATIONS OF CERIUM.

	Formula.	Molecular Weight.	Per cent. of Cerium.
Oxide	Ce_2O_3	329	85.41
Chloride	Ce_2Cl_6	493.4	56.95
Nitrate	$\text{Ce}_2(\text{NO}_3)_6 \cdot 12\text{H}_2\text{O}$	869	32.34
Sulphate	$\text{Ce}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	781	88.44
Carbonate	$\text{Ce}_2(\text{CO}_3)_3 \cdot 9\text{H}_2\text{O}$	628	45.10
Oxalate	$\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$	707	89.74

CHAPTER VII.**COPPER.****CUPRUM.**

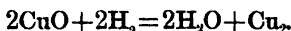
Cu. 63.2.

Sp. gr. 8.9.

Occurs chiefly native and in combination with sulphur. Reduced by a smelting process. To illustrate the reduction from the oxide, the following experiment may be tried:

Exp. 72. Introduce two or three Gm. of fine copper oxide into a hard glass tube 15 Cm. long and 1 Cm. in internal diameter, to which

smaller tubes are connected at each end by perforated corks. Through one of these pass a current of dried hydrogen from a generator. When the air has been driven out through the other, which should be drawn to a coarse point, light the escaping gas. Now heat the large tube with a Bunsen burner, moving it backwards and forwards to avoid cracking. Finally increase the heat and observe the gradual formation of bright metallic copper and the escape of steam along with the gas from the delivery tube. (See Fig. 17.) The reaction taking place is this:



Copper is recognized as such by its physical properties, hardness, density, color, etc., or by chemical tests after solution.

The chief analytical reactions of copper salts are as follows:

1°. Hydrogen sulphide precipitates from neutral, acid or alkaline solutions black copper sulphide, CuS . This is not soluble in dilute sulphuric or hydrochloric acid, but readily in nitric.

It is also soluble in hot solution of potassium cyanide. It is insoluble in alkaline sulphides, excepting ammonium sulphide, which dissolves it slightly.

2°. Ammonium hydrate added to a solution of a copper salt, as the sulphate, precipitates light blue copper hydrate, $\text{Cu}(\text{OH})_2$, which dissolves in excess forming a deep blue liquid containing copper ammonium sulphate, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$.

3°. Potassium or sodium hydrate precipitates, in the cold, copper hydrate; on boiling, this is converted into black copper oxide, CuO .

4°. Metallic iron or zinc precipitates copper from solutions of its salts. A piece of iron immersed in a solution of a copper salt slightly acidified, soon becomes coated. A piece of zinc placed in an acidified copper solution contained in a platinum dish causes the total precipitation of the copper as a firm coating on the dish.

5°. Potassium ferrocyanide precipitates from neutral or slightly acid solutions of copper salts, copper ferrocyanide, Cu_2FeCy_6 , reddish brown.

Copper is used in numerous alloys, in wire for electric circuits, and in water-baths, stills, pans, boilers and drying ovens for laboratory or household operations.

It is corroded by the action of most acid substances, especially when hot, and also by alkalis. Hence, such substances should not be heated in contact with it.

Copper is used in the direct preparation of a few compounds.

PREPARATIONS OF COPPER.

	Formula.	Molecular Weight.	Per cent. of Copper.
Oxide (ous).....	Cu_2O	142.4	88.76
Oxide (ic).....	CuO	79.2	79.79
Chloride (ous).....	Cu_2Cl_2	197.2	64.09
Chloride (ic).....	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	170	87.17
Sulphide (ous).....	Cu_2S	158.4	79.79
Sulphide (ic).....	CuS	95.2	66.28
Sulphate.....	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	249.2	25.86
Phosphide.....	Cu_3P_2	251.6	75.85
Phosphate.....	$\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$	433.6	43.72
Nitrate.....	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	241.2	26.20
Carbonate (basic).....	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	220.4	57.85
Arsenite.....	CuHAsO_3	187.2	33.76
Acetate.....	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$	199.2	81.72
— ammon. sulphate.....	$\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$	245.2	25.77

LEAD.

PLUMBUM.

Pb. 206.5.

Sp. gr. 11.4.

From its chief native compound, the sulphide, *galena*, it is obtained by simple metallurgical operations. Its physical properties are characteristic, and when pure it can readily be recognized. It forms a part of many alloys, in which it may be found by special methods. It is thrown out from its combinations by zinc and other metals, as illustrated in this experiment:

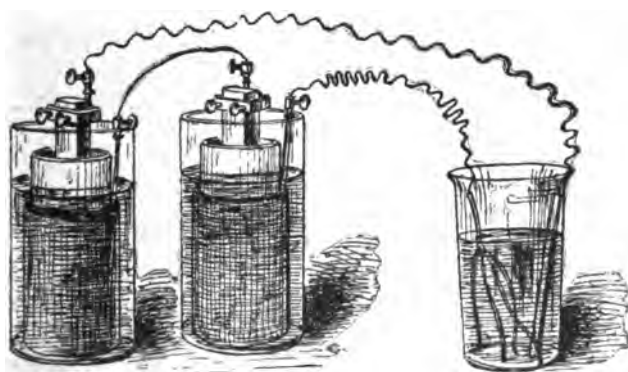


FIG. 18.

Exp. 73. In a dilute solution of lead acetate, acidulated slightly with acetic acid, suspend several pieces of sheet zinc. After a time these become coated with small crystals of metallic lead, to which others forming attach themselves, producing in time the so-called *lead tree*.

The amounts of zinc dissolved and of lead precipitated are proportional to their atomic weights.

An interesting modification of the experiment may be made in this way: Twist the ends of several narrow strips of lead together so as to roughly resemble the branches of a tree; attach the "trunk" end to a copper wire, and immerse in a strong solution of lead acetate containing a little nitric acid. Fasten another wire to a strip of sheet lead and place this in the same solution, but not touching the first. Now attach both wires to the poles of a battery, the "tree" to the zinc pole. In a few minutes brilliant spangles of lead will shoot out all over the tree and soon cover it. The apparatus is shown in Fig. 18.

Among the tests for lead salts the following are the most important:

1°. Hydrogen sulphide precipitates from neutral, slightly acid or alkaline solutions black lead sulphide, PbS . In presence of much free hydrochloric acid lead chloro-sulphide, a red compound, is first thrown down. Excess of H_2S finally decomposes this. The precipitate dissolves in dilute hot nitric acid as lead nitrate; by the strong acid it is oxidized to lead sulphate.

2°. Sulphuric acid precipitates white lead sulphate, PbSO_4 , from solutions of lead salts. The precipitate is but slightly soluble in dilute acids; in strong nitric, sulphuric and hydrochloric acids it may be dissolved by boiling. It is soluble in solutions of several ammonium salts, but dilute sulphuric acid reprecipitates it. The solubility in water may be further lessened by addition of alcohol.

3°. Potassium chromate precipitates yellow lead chromate, PbCrO_4 , soluble in nitric acid.

4°. Hydrochloric acid precipitates lead chloride, PbCl_2 , soluble in boiling water completely, and slightly soluble in cold. From the solution in hot water the PbCl_2 settles out on cooling in white glistening needles, very characteristic.

PREPARATIONS OF LEAD.

	Formula.	Molecular Weight.	Per cent. of Lead.
Oxide (ous).....	PbO	222.5	92.80
Oxide (ous, ic).....	Pb_2O_3	683.5	90.63
Oxide (ic).....	PbO_2	288.5	86.58
Chloride.....	PbCl_2	277.8	74.10
Bromide.....	PbBr_2	366.1	56.40
Iodide.....	PbI_2	459.7	44.92
Sulphide.....	PbS	288.5	86.58
Sulphate.....	PbSO_4	302.5	68.26
Nitrate.....	$\text{Pb}(\text{NO}_3)_2$	330.5	62.48
Chromate.....	PbCrO_4	322.5	64.08
Carbonate ("white lead").....	$2(\text{PbCO}_3) \cdot \text{Pb}(\text{OH})_2$	773.5	80.09
Acetate.....	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	378.5	54.55
Acetate (basic).....	$2\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO}$	871.5	71.08

Lead is used in evaporating pans for concentrating sulphuric acid, in the lining of laboratory sinks, in dishes for heating sulphuric acid and fluorspar for etching purposes, and generally in water and waste pipes in buildings.

SILVER.

ARGENTUM.

Ag. 107.7.

Sp. gr. 10.6.

Found native and in various combinations, but chiefly as sulphide. Extracted by amalgamation, after preliminary conversion into chloride. Pure silver is prepared by reducing the chloride, by fusing it with dry sodium carbonate. It dissolves most readily in nitric acid. The following tests serve to identify silver in its compounds:

1°. Hydrogen sulphide precipitates silver sulphide, Ag_2S , from solutions of silver salts. The precipitate is black, is insoluble in dilute acids, but is decomposed by strong, hot nitric acid.

2°. Potassium chromate precipitates from neutral solutions red silver chromate, Ag_2CrO_4 , which is soluble in a large excess of the precipitant and in ammonium hydrate.

This is a delicate reaction.

3°. Hydrochloric acid, or a soluble chloride, throws down from silver solutions a white, curdy precipitate of silver chloride, AgCl , which is readily soluble in ammonium hydrate. It is also soluble in solutions of sodium thiosulphate, potassium cyanide, and, to some extent, in concentrated boiling hydrochloric acid and solutions of alkali chlorides. Exposed to the light it changes color, as may be illustrated by this experiment.

A little chloride is precipitated, thrown on a filter and washed with water, the filter is opened out and the moist mass spread over it. If this is now exposed to bright sunlight it becomes violet immediately; in diffuse light more slowly. In time the color deepens to black. This change is probably due to the formation of new compounds containing less chlorine, as Ag_2Cl_2 , and upon this reducing action of light depends the use of silver salts in photography.

Silver is chiefly used as coin, for various vessels and utensils, for plating, in fine wire for surgeons' use, and in the laboratory for crucibles and dishes in which alkalies are fused, or strongly heated.

PREPARATIONS OF SILVER.

	Formula.	Molecular Weight.	Per cent. of Silver.
Oxide (ous).....	Ag_2O	231.4	93.06
Oxide (ic).....	Ag_2O_2	247.4	87.07
Chloride.....	AgCl	148.1	75.26
Bromide.....	AgBr	187.5	57.44
Iodide.....	AgI	234.8	45.96
Cyanide.....	AgCy	133.7	80.55
Sulphide.....	Ag_2S	247.4	87.06
Sulphate.....	Ag_2SO_4	311.4	69.17
Nitrate.....	AgNO_3	169.7	68.46
Carbonate.....	Ag_2CO_3	275.4	78.21

MERCURY.

HYDRARGYRUM.

[QUICKSILVER.]

Hg. 200.

Sp. gr. 13.596.

Found native, but chiefly as the sulphide, *cinnabar*. It is extracted from this ore by distillation. It is the only common metal liquid at ordinary temperatures, and by this fact is readily recognized.

An important characteristic of mercury is its property of *alloying* readily with many metals, which can be illustrated in this way:

Exp. 74. Clean a piece of copper, or a common cent, by rubbing it with nitric acid and washing with water, and place on it a drop of mercury. This soon spreads over the whole surface, imparting to it a white color. By heating the copper the mercury volatilizes, leaving it as before. Similar compounds are formed with silver, gold, cadmium, bismuth and other metals, and are called *amalgams*.

The following tests serve to show the presence of mercury in compounds:

1°. Dry sodium carbonate heated with dry mercury compounds, in a glass tube, decomposes them, liberating the metal which collects in droplets on the cooler upper portion of the tube.

Where the quantity is small it may be seen only after collecting it, by rubbing the tube with a platinum wire or a piece of twisted filter paper.

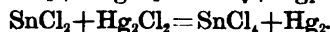
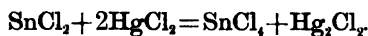
2°. A piece of copper immersed in solutions of mercuric salts, acidulated with hydrochloric acid, becomes covered with a white coating, as explained above.

3°. Hydrogen sulphide precipitates the mercury from solutions containing it, as black sulphide, HgS , from mercuric salts, and HgS mixed with metallic mercury from mercurous.

From solutions of mercuric salts the hydrogen sulphide throws down first a *white* precipitate; on adding more of the reagent the color becomes reddish and finally black. This change of color is due to the formation of precipitates containing mercuric sulphide and the salt in solution. The latter being in excess at first gives its color to the mixture; as more sulphide is formed the black obscures the white, passing through the several shades observed, until the precipitate contains only HgS . This is insoluble in hydrochloric and nitric acids. The latter, by long boiling, converts it into a white compound, $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgS}$, likewise insoluble.

Aqua regia dissolves the HgS readily.

4°. Stannous chloride added to a solution of mercuric chloride produces a precipitate of mercurous chloride, Hg_2Cl_2 , which is white. An excess of the reagent produces a gray precipitate from the separation of some metallic mercury, in a very fine condition, by further reduction. These equations show this:



5°. Hydrochloric acid precipitates white mercurous chloride, Hg_2Cl_2 , from solutions of mercurous salts. This precipitate is not soluble in dilute acids. It is converted by ammonia water into a black compound, Hg_2ClNH_2 .

Mercury is used for filling thermometers and barometers, in the extraction of gold and silver by amalgamation, in alloys used by dentists, and in the direct preparation of several pharmaceutical compounds.

PREPARATIONS OF MERCURY.

	Formula.	Molecular Weight.	Per cent. of Mercury.
Oxide (ous).....	Hg_2O	416	96.15
Oxide (ic).....	HgO	216	92.59
Chloride (ous).....	Hg_2Cl_2	470.8	84.96
Chloride (ic).....	HgCl_2	270.8	73.85
Chloride (ammoniated).....	HgClNH_2	251.4	79.55
Bromide (ic).....	HgBr_2	359.6	55.61
Iodide (ous).....	Hg_2I_2	653.2	61.24
Iodide (ic).....	HgI_2	453.2	44.13
Cyanide (ic).....	HgCy_2	252	79.36
Sulphide (ous).....	Hg_2S	432	92.59
Sulphide (ic).....	HgS	232	86.20
Sulphate (ous).....	Hg_2SO_4	496	80.64
Sulphate (ic).....	HgSO_4	296	67.56
Sulphate (basic).....	$\text{HgSO}_4 \cdot 2\text{HgO}$	728	82.41
Nitrate (ous).....	$\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	560	71.43
Nitrate (ic).....	$\text{Hg}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$	468	42.73
Carbonate (ous).....	Hg_2CO_3	460	86.95
Carbonate (basic).....	$\text{HgCO}_3 \cdot 3\text{HgO}$	908	88.10

BISMUTH.**BISMUTHUM.**

Bi. 207.5.

Sp. gr. 9.8.

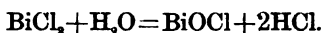
Bismuth occurs chiefly native, mixed with various gangues. From these it is separated by melting.

In pure form it is easily recognized by its brittleness and peculiar grayish color with reddish reflexions.

In its compounds it may be recognized by these tests:

1°. Hydrogen sulphide precipitates bismuth compounds as black sulphide, Bi_2S_3 , which is not soluble in dilute acids or alkalies. It is decomposed by strong, hot nitric acid.

2°. Water gives white precipitates with acid solutions of most bismuth salts. Bismuth trichloride in hydrochloric acid is precipitated according to this equation:



This is a very characteristic test.

3°. Ammonium hydrate produces in solutions of bismuth salts a precipitate of bismuth hydrate, BiOOH , insoluble in excess of the reagent.

Bismuth is used in several alloys. It lowers the fusing point and imparts hardness.

It is used also in the direct preparation of several of its salts.

PREPARATIONS OF BISMUTH.

	Formula.	Molecular Weight.	Per cent. of Bismuth.
Oxide	Bi_2O_3	468	89.63
Chloride	BiCl_3	313.7	66.14
Oxychloride	BiOCl	253.9	80.15
Nitrate	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	493.5	42.91
Subnitrate	$\text{BiONO}_3 \cdot \text{H}_2\text{O}$	303.5	63.36
Sulphide	Bi_2S_3	511	81.21
Subcarbonate	$2(\text{BiO})\text{CO}_3 \cdot \text{H}_2\text{O}$	525	79.05
Citrate	$\text{BiC}_6\text{H}_5\text{O}_7$	396.5	52.33
— ammon. citrate			

CADMIUM.**CADMIUM.**

Cd. 112.

Sp. gr. 8.6.

Occurs most abundantly as sulphide. The metal is obtained by converting the sulphide into oxide by heat, and then reducing this with coal or charcoal.

It resembles lead in many respects, and enters into the composition of several alloys.

In compounds its presence may be shown by the following tests:

1°. Hydrogen sulphide throws down bright yellow cadmium sulphide, CdS , from neutral, acid or alkaline solutions. This will not dissolve in solution of potassium cyanide, but will in dilute sulphuric acid. (Differs by this behavior from copper sulphide.)

2°. Ammonium hydrate precipitates cadmium hydrate, $\text{Cd}(\text{OH})_2$, from solutions, but this dissolves in excess to a colorless liquid. The same precipitate is produced by sodium hydrate, but an excess will not dissolve it.

PREPARATIONS OF CADMIUM.

	Formula	Molecular Weight.	Per cent. of Cadmium.
Oxide	CdO	128	87.5
Chloride	$\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$	218.8	51.18
Bromide	$\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$	343.6	32.60
Iodide	CdI_2	365.2	30.66
Sulphide	CdS	144	77.77
Sulphate	$3(\text{CdSO}_4) \cdot 8\text{H}_2\text{O}$	768	43.74
Nitrate	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	308	36.36

CHAPTER VIII.

ARSENIC.

ARSENUM.

As. 75.

Sp. gr. 4.7 to 5.7.

Arsenic occurs native, and combined as sulphide. The "arsenic" of commerce is the oxide, As_2O_3 , which is formed as a by-product in several metallurgical operations. To show the ready reduction of this the student should try the following experiment:

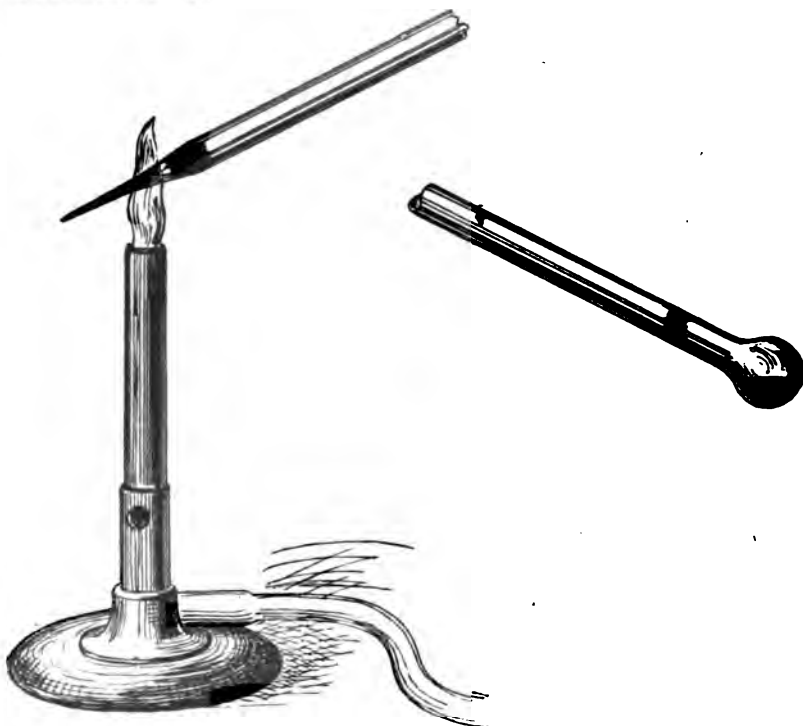
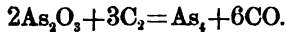


FIG. 19.

Exp. 75. A little of the powder is placed in the bottom of a hard glass tube, and above it some small fragments of charcoal. The tube

should be slightly narrowed, so as to hold the latter a short distance above the arsenous oxide. Now heat the tube; the oxide volatilizes and comes in contact with the hot charcoal, which decomposes it in this way:



For the complete success of this experiment the charcoal should be freshly burnt, and should be hot before the oxide commences to volatilize. The pure arsenic is deposited as a dark metallic ring above the charcoal. Arsenites, and other compounds heated in a bulb tube with a mixture of equal parts of dry sodium carbonate and potassium cyanide, are reduced, giving a black ring. (See Fig. 19.)

Arsenic compounds are recognized by these tests:

1°. The white oxide, the most usual form in which it appears in commerce, is but slightly soluble in cold water. It is more soluble in hot water, and can be readily dissolved by hydrochloric acid, and by solutions of sodium and potassium hydrates.

2°. Hydrogen sulphide precipitates acid solutions of arsenous compounds, as arsenous sulphide, As_2S_3 . Neutral and alkaline solutions are not precipitated.

Solutions of arsenic compounds are first reduced to arsenous, with separation of sulphur, and then precipitated as before. The yellow precipitate is soluble in solution of alkalies and alkaline sulphides. In the latter case *sulpharsenites* are formed, as Na_2AsS_2 .

3°. Silver nitrate produces in solutions of normal arsenites a yellow precipitate of silver arsenite, Ag_3AsO_3 . In a water solution of arsenous oxide this precipitate is formed after the addition of a few drops of ammonium hydrate. It is soluble in an excess of the latter, in nitric acid, and in ammonium nitrate solution. Under similar circumstances silver nitrate produces in solutions of arsenic compounds (arsenates) a brick red precipitate of silver arsenate, Ag_3AsO_4 . The properties of this precipitate are quite similar to those of the arsenite. The solution of the latter in ammonia, boiled, deposits silver, while that of the arsenate does not.

4°. A piece of bright copper wire or foil heated with a solution of arsenous oxide in hydrochloric acid becomes coated with a gray metallic film of copper arsenide. When heated with ammonium hydrate solution this film peels off. To obtain the film from solutions of arsenic oxide it is necessary to add a much larger excess of strong hydrochloric acid.

This is known as Reinsch's test, but it must be used with caution, as several other metals treated in this way give similar films.

5°. A small amount of copper sulphate solution added to a solution of arsenous oxide, in an excess of sodium or potassium hydrate, produces a blue fluid, and throws down, on boiling, a bright red precipitate of copper suboxide, Cu_2O . This test is valuable to distinguish between

arsenous and arsenic oxides, but cannot be accepted as a final one in testing a body of unknown origin, as many organic substances have the same reducing action on copper sulphate in strong alkaline solution. To make the experiment a success the alkali must be in large excess.

6°. Nascent hydrogen acts on all arsenic compounds, reducing them and liberating arsenetted hydrogen, AsH_3 . To detect arsenic by this method fit a flask of about 300 C.c. capacity with a funnel tube and delivery tube, and to the latter attach a drying tube of the usual form, containing calcium chloride. To this is attached a tube of hard glass, having an internal diameter of about 8 Mm., drawn to a point, as shown in the cut below.

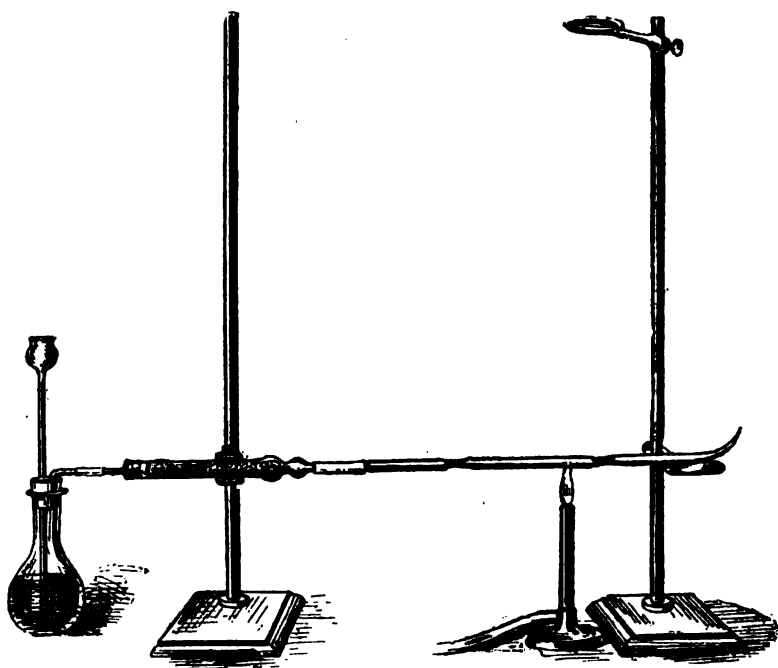
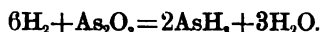


FIG. 20.

Place in the flask some fragments of pure zinc and about 100 C.c. of pure dilute sulphuric acid (1 to 5). Hydrogen is liberated; *when this has completely expelled the air* light it at the end of the hard glass tube.

Now pour the neutral or acid solution containing arsenic through the funnel tube, a very little at a time. AsH_3 is produced according to this equation:



It escapes with the excess of hydrogen, and burns with a bluish white flame, somewhat characteristic. If a piece of cold porcelain is

held now in the flame it lowers the temperature and limits the supply of air, so that the arsenic cannot burn to oxide but is deposited in the free state as a black metallic spot.

These spots are readily volatile, and they dissolve in a solution of sodium hypochlorite.

If the heat of a Bunsen burner is applied to the tube (as shown by the cut), decomposition takes place there, and a stain is found in the tube, at some distance beyond the hot part.

If the arsenic is present in small amount only, no stain can be obtained on the porcelain as long as heat is applied to the tube.

This test was first proposed by Marsh, and is one of the best known for the detection of very minute quantities of arsenic.

In important cases it is necessary to test the escaping gas thoroughly by the methods just given, before adding the solution under investigation. It is also necessary to distinguish between arsenic and antimony, as will be explained below.

PREPARATIONS OF ARSENIC.

	Formula.	Molecular Weight.	Per cent. of Arsenic.
Oxide (ous).....	As_2O_3	198	75.75
Oxide (ic).....	As_2O_5	230	65.21
Chloride.....	AsCl_3	181.2	42.89
Iodide.....	AsI_3	454.8	16.49
Sulphide (realgar).....	As_2S_3	214	70.09
Sulphide (ous).....	As_2S_4	246	80.97
Sulphide (ic).....	As_2S_5	310	48.39

ANTIMONY.

ANTIMONIUM.

[STIBIUM.]

Sb. 120.

Sp. gr. 6.7.

Occurs usually as dark gray sulphide, Sb_2S_3 , *stibnite*. The metal is obtained by heating this with iron, or by oxidizing it by roasting and then reducing with charcoal. It is exceedingly brittle, crystalline, and has a characteristic gray color.

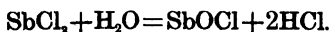
The metal is converted by strong nitric acid into an insoluble oxide, white.

Hydrochloric acid does not attack it, but it dissolves readily in *aqua regia*.

Exp. 76. Let the student boil about half a Gm. of the fine powder in *aqua regia* contained in a small flask, replacing from time to

time the acid lost by evaporation. When solution is complete the liquid should be transferred to an evaporating dish and concentrated until a thick syrup remains. This consists chiefly of the chloride, SbCl_3 , called *butter of antimony*.

By pouring this into water a white precipitate of the oxychloride is thrown down.



The chief analytical tests are these:

1°. Hydrogen sulphide precipitates orange red antimonious sulphide from acid solutions of antimonious compounds. Alkaline or neutral solutions are only partially thrown down.

The precipitate is soluble in a solution of potassium hydrate or of an alkaline sulphide. In the latter case a sulphantimonate is formed, as $(\text{NH}_4)_3\text{SbS}_4$.

Antimonic compounds are precipitated as orange red antimonic sulphide, Sb_2S_5 , by hydrogen sulphide.

2°. Compounds of antimony treated in the Marsh apparatus, as described under arsenic, yield *antimonetted hydrogen*, SbH_3 , which in many points is similar to the corresponding arsenic compound AsH_3 .

These points of difference may be noted.

(a) The imperfect combustion of the SbH_3 produces a stain on porcelain, which is blacker than the arsenic stain and but slightly lustrous.

(b) This stain is not soluble in a hypochlorite solution (or partially soluble after a long contact).

(c) The antimony stain is less volatile than that from arsenic. (d) If the stain be produced in the tube it is immediately above or on both sides of the flame in the case of antimony, and beyond it in the case of arsenic. (e) If the gases are led through a wide tube containing KOH in small pieces the AsH_3 would pass unchanged, and could be recognized by its stain, while the SbH_3 would be decomposed with precipitation of the metal on the KOH.

3°. Metallic zinc decomposes solutions of antimony compounds free from nitric acid, precipitating the metal as a black mass. If the experiment is tried in platinum, or if a piece of platinum foil is dropped into the glass vessel containing the zinc and antimony solution and some hydrochloric acid added, the platinum becomes covered with a black deposit of metallic antimony. The stain is removed readily by nitric acid.

PREPARATIONS OF ANTIMONY.

	Formula.	Molecular Weight.	Per cent. of Antimony
Oxide (ous).....	Sb_2O_3	288	83.83
Oxide (ic).....	Sb_2O_5	320	75.00
Chloride (ous).....	SbCl_3	228.2	53.05
Oxychloride.....	SbOCl	171.4	70.01
Chloride (ic).....	SbCl_5	297	40.40
Sulphide (ous).....	Sb_2S_3	336	71.43
Sulphide (ic).....	Sb_2S_5	400	60.00
— potass. tartrate.....	$2(\text{KSbOC}_4\text{H}_4\text{O}_6)\cdot\text{H}_2\text{O}$	664	36.14

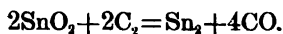
TIN.

STANNUM.

Sn. 117.7

Sp. gr. 7.3.

Occurs usually as oxide or "tinstone," SnO_2 . After a preliminary purification the ore is reduced with charcoal.



Exp. 77. To illustrate the reduction a very small amount of the artificial oxide can be mixed with like amounts of dry sodium carbonate and potassium cyanide, and heated strongly with the reducing flame of the blow-pipe. In a few minutes small globules of metallic tin can be seen in the fused mass. The potassium cyanide here acts as the reducing agent, becoming converted into cyanate.

Pure tin can generally be recognized by its physical properties. Nitric acid converts it into metastannic acid, $\text{Sn}_3\text{H}_{10}\text{O}_{15}$, which heated, leaves the dioxide, SnO_2 .

Tin is soluble in hydrochloric acid forming stannous chloride, and in *aqua regia* forming stannic chloride.

The chief analytical tests for tin compounds are these:

1°. Hydrogen sulphide in excess precipitates from acid or neutral solutions of stannous compounds, brown stannous sulphide, SnS , and from solutions of stannic salts, light yellow stannic sulphide, SnS_2 . Alkaline solutions yield no precipitates.

These precipitates are soluble in potassium or sodium hydrate and in yellow ammonium sulphide.

2°. Mercuric chloride is reduced by solutions of stannous chloride to insoluble mercurous chloride, Hg_2Cl_2 . If the stannous chloride is in large excess metallic mercury will be thrown down.

3°. Metallic zinc, placed in solutions of tin compounds containing hydrochloric acid, precipitates the tin in the metallic form as a black spongy mass. If the experiment is tried in platinum the latter is not colored, as is the case with antimony.

Tin is used in several alloys, as a coating for sheet-iron in so-called "tinplate" or "tinware," as coating for copper in stills and boilers, which are thereby rendered less liable to corrosion; in "block tin" tubing intended to convey mineral waters or other liquids used for drinking, and elsewhere in a similar manner because of its insolubility in most substances with which it could come in contact. It is also used in the direct preparation of many tin compounds.

PREPARATIONS OF TIN.

	Formula.	Molecular Weight.	Per cent. of Tin.
Oxide (ous)	SnO	133.7	88.08
Oxide (ic)	SnO_2	149.7	78.62
Chloride (ous)	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	224.5	52.42
Chloride (ic, fuming)	SnCl_4	259.3	45.40
Sulphide (ous)	SnS	149.7	78.62
Sulphide (ic)	SnS_2	181.7	64.77

GOLD.

AURUM.

Au. 196.2.

Sp. gr. 19.33.

Gold occurs usually in the free state mixed with gangue, from which it is extracted by amalgamation.

The peculiar yellow color, and density are characteristic of the metal. It is insoluble in nitric or hydrochloric acid, but dissolves in *aqua regia*. The compounds may be tested in this way:

1°. Gold solutions containing a little hydrochloric acid, not nitric, are reduced by solution of ferrous sulphate, the gold precipitating as a fine brown powder, which remains for a time suspended, imparting a dark blue color to the liquid.

2°. Stannous chloride solution containing a little stannic chloride throws down from gold solutions a fine purple precipitate, known as the *purple of Cassius*. This is an exceedingly delicate reaction.

PREPARATIONS OF GOLD.

	Formula.	Molecular Weight.	Per cent. of Gold.
Oxide	Au_2O_3	440.4	89.10
Chloride (ic)	AuCl_3	302.4	64.88
— sodium chloride	$\text{AuCl}_3 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}$	396.8	49.44
Cyanide (ous)	AuCy	222.2	88.29

Besides its well known uses for coin, jewelry and plate, gold is employed in fine powder and foil by dentists, as wire by surgeons, and occasionally it is used by chemists in crucibles for special purposes.

Fine weights and other implements of research are frequently plated with gold.

PLATINUM.

PLATINUM.

Pt. 194.8.

Sp. gr. 21.5.

Platinum occurs, alloyed with several other rare metals, in the free state, and is separated and purified by rather complicated processes. It is a white metal, insoluble in nitric or hydrochloric acid, but is slowly soluble in *aqua regia*. The following test is characteristic of platinum:

Solutions of potassium and ammonium chlorides precipitate platinum solutions containing a little hydrochloric acid, as yellow double chloride of potassium and platinum, or ammonium and platinum, $\text{PtCl}_4 \cdot 2\text{KCl}$ or $\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$. By collecting and igniting the precipitates the first leaves spongy platinum and KCl, the second spongy platinum alone.

Metallic platinum is used in coin (Russia), in weights and instruments of precision, and in foil, wire, dishes, funnels, crucibles, etc., for laboratory purposes.

It is not safe to heat it in contact with compounds of the heavy metals, as gold, silver or lead, as these substances form with platinum easily fusible alloys. Solutions containing *aqua regia*, or which liberate chlorine, cannot be evaporated in platinum dishes.

Substances containing free carbon (or excess of organic carbon) and phosphates must be ignited with great care in platinum dishes, as there is danger of liberation of free phosphorus, which combines quickly with platinum. When allowable, ammonium nitrate may be added before beginning the ignition of such mixtures.

Fixed alkalis must not be fused in platinum.

PREPARATIONS OF PLATINUM.

	Formula.	Molecular Weight.	Per cent. of Platinum.
Chloride	PtCl_4	386.4	57.90
— potass. chloride	$\text{PtCl}_4 \cdot 2\text{KCl}$	485.2	40.15
— sodium chloride	$\text{PtCl}_4 \cdot 2\text{NaCl} \cdot 6\text{H}_2\text{O}$	561.2	34.71
Iodide	PtI_4	701.2	27.78
— potass. cyanide	$\text{PtCl}_4 \cdot 2\text{KCyanide} \cdot 3\text{H}_2\text{O}$	449.6	43.33

MOLYBDENUM.**MOLYBDÆNUM.**

Mo. 96.

Sp. gr. 8.6.

This is a rare metal, occurring usually as sulphide. It is obtained by reducing the oxide in a current of hydrogen.

It forms molybdates, of which several have uses in analytical chemistry.

These are recognized as follows:

1°. A solution of a molybdate containing a little hydrochloric acid changes color on addition of metallic zinc. It becomes at first blue, then green, and finally brown.

2°. Hydrogen sulphide turns an acid solution blue; when added in excess it precipitates brown molybdenum sulphide, MoS_3 .

3°. Solution of a phosphate added to an excess of solution of ammonium molybdate containing nitric acid, produces a yellow crystalline precipitate of ammonium phospho-molybdate, the composition of which is somewhat variable.

TUNGSTEN.**WOLFRAMIUM.**

W. 184.

Sp. gr. 19.13.

Tungsten occurs usually as tungstate of iron, manganese, calcium or lead.

The metal can be obtained by reduction of the oxide by means of hydrogen.

Many compounds are known in which tungsten plays the part of an acid. Sodium tungstate is the most important of these. The tungsten salts are not important.

Tests for tungstates:

1°. Metallic zinc produces in a solution of a tungstate, containing hydrochloric acid, a characteristic deep blue color.

2°. Ammonium sulphide added to a solution of an alkali tungstate produces no precipitate. If hydrochloric acid is added, brown tungstic sulphide, WS_3 , is thrown down.

3°. Potassium ferrocyanide produces a red color in an acidified solution of a tungstate.

PART II.

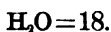
SYNTHETICAL CHEMISTRY.

INORGANIC PREPARATIONS.

CHAPTER IX.

WATER.

AQUA.



The Pharmacopoeia of the United States defines "aqua" as "natural water in its purest attainable state." It must be colorless, clear, inodorous, and tasteless. Should not contain more than a few grains of fixed impurities in one wine-gallon; and not more than traces of organic matter.

Spring water usually contains inorganic salts, consisting chiefly of the chlorides, sulphates and carbonates of calcium, magnesium, etc. Such water is called *hard water*, because when used with soap it produces insoluble compounds, which cause a sense of harshness. Hard water can be rendered less so by boiling it, because the calcium and magnesium carbonates, which are held in solution by the carbonic acid present, deposit as soon as that acid is expelled by the heat. Spring water is generally unfit for pharmaceutical uses on account of the mineral impurities it contains.

Well water often contains organic matter derived from sewage, etc., especially in thickly inhabited places, and must not be used unless careful examination shows it to be sufficiently pure. Water contaminated with organic substances contains ammonia. The presence of organic matter in sufficient quantity to impart odor to the water should at once condemn it. Where pure water is not obtainable for ordinary purposes, small quantities of organic impurities may be partially

removed by adding a little alum; the ammonia and carbonates present cause the precipitation of aluminium hydrate, which, as it settles, carries other impurities with it.

Rain water is pure if collected in clean vessels as it descends from the clouds after the rain has continued long enough to purify the atmosphere from dust, etc. Falling off roofs and collected from the conduits in the usual way it is rarely pure.

Ice, when melted, affords a comparatively pure water.

River and lake water, containing usually but small amounts of calcium and magnesium salts, is called *soft water*, and is frequently pure enough for most purposes; it may, however, contain both organic and inorganic impurities.

Uses.—Water is indispensable in medicine, pharmacy, chemistry, as well as in the household economy. It is the best solvent and diluent we have, being abundant, and capable of dissolving a great variety of substances. It is, moreover, chemically indifferent or neutral to most substances, and hence affords a means of reducing water-soluble substances to a liquid condition without otherwise altering their properties, and can be freely used to facilitate many chemical reactions.

Tests.—The residue left on evaporation of one liter of the water should be less than 0.10 Gm.

Mix 100 C.c. of the water with 10 C.c. of diluted sulphuric acid; heat to boiling; then add enough solution of permanganate of potassium (1 part to 1000 parts of distilled water) to give to the mixture a distinct rose-red color; then boil for five minutes. The color will not be entirely destroyed by this treatment unless more than traces of organic matter be present.

DISTILLED WATER.

AQUA DESTILLATA.

Water, a convenient quantity.

Put the water into a suitable still of copper or tinned iron, the still to be about two-thirds filled. Connect it with a suitable condenser, and distil. The first portion that passes over is to be rejected, being contaminated with impurities taken up in its passage through the apparatus, and containing also any carbonic acid or other volatile substances which may have been present in the water. When only about one-fifth or one-sixth of the water remains in the still, the process is to be arrested in order to prevent possible contamination with products of decomposition of organic substances by overheating.

Properties.—Colorless, clear, inodorous, tasteless. Boils at 100° C. (212° F.); freezes at 0° C. (32° F.); assumes its maximum density at +4° C. (39° F.). Specific gravity = 1 at +4° C. (39° F.).

Tests.—Should yield no residue on evaporation. In applying the permanganate test described above to distilled water, the rose-red tint should not only remain after five minutes' boiling, but should not be entirely destroyed, even after ten hours' standing in a covered vessel subsequent to the boiling.

The following additional tests are prescribed:

It should not be affected by test solutions of chloride of barium (sulphate), nitrate of silver (chloride), oxalate of ammonium (calcium), or mercuric chloride, with or without the subsequent addition of carbonate of potassium (ammonia and ammonium salts).

ACIDS.

ACIDA.

Acids may be termed the salts of hydrogen. Thus, hydrochloric acid is hydrogen chloride; nitric acid is hydrogen nitrate, etc., in which the hydrogen is replaceable by a positive element or group, as by a metal.

The common acids are sour to the taste, turn blue litmus red, and are neutralized by bases, forming salts. Distinction is commonly made between "hydracids," which contain no oxygen, and "oxyacids," which contain oxygen.

The acids are extensively used in the preparation of other compounds. In the employment of acids for such purposes care should be taken to see that they are of the proper strength and purity—matters which are too often neglected.

The stronger acids being highly corrosive, must be handled with special caution. Large vessels, as carboys, containing acids, must be kept in a place where their accidental breakage will not cause serious damage. Special carboy stands as well as trunnions are therefore employed in laboratories where large quantities of acids are consumed.

When the quantities used are not too great, the most convenient and safe packages are the common "half-gallon acid bottles," with well ground glass stoppers. The removal of the glass stopper when it has become fast in the neck of an acid bottle is always attended with the risk of breakage and other more serious consequences. A caution to proceed deliberately is therefore always in order. Gently tapping the stopper with a wooden block or handle, warming the neck of the bottle with a cloth dipped in hot water, or by cautiously turning it over the flame of a spirit lamp or Bunsen burner, and inverting the bottle in a vessel containing enough warm water to cover the neck well, are among the best means of loosening the stopper sufficiently to render the application of the stopper wrench successful. When the stopper is

being removed, the face should be turned away from the bottle, especially if the latter is warm, because there may possibly be a rush of vapor from it.

The respective strengths of the official acids of different countries unfortunately vary greatly. This fact is to be taken into consideration in using working formulæ of foreign source.

In the British Pharmacopœia the acids in common with all other liquids are prescribed by measure; in all other pharmacopœias they are prescribed by weight.

Manufacturers in this country generally indicate the strength of acids in degrees Beaumé. In other cases they do not specify the strength at all, as for instance in the case of "No. 8" acetic acid. If pharmacists would insist that all packages containing acids should bear labels indicating the specific gravity (not the degrees Beaumé) and the percentage of absolute acid claimed for the contents, and if they would refuse to accept any package not so labeled, the results could not but be beneficial to all parties concerned, as well as to the art. In ordering acids it is safest to specify the strength in per cent. of absolute acid.

CHAPTER X.

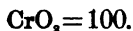
OXIDES AND HYDRATES.

Chromic anhydride and arsenous anhydride are the only acid-forming oxides here described.

The basic oxides of calcium, magnesium, zinc, iron, copper, mercury, silver, bismuth and antimony, are all insoluble in water. They are prepared by calcining the carbonates, by oxidizing the metals, or by precipitation of soluble salts by means of alkali hydrates.

CHROMIC ANHYDRIDE.**ACIDUM CHROMICUM.**

[CHROMIC ACID.]



Potassium bichromate.....	30 Gm.
Sulphuric acid.....	57 C.c.
Distilled water, sufficient.	

Dissolve the potassium bichromate in a mixture of 42 C.c. of the acid, and 50 C.c. of water. Set aside for twelve hours, and decant the liquor from the crystals of acid potassium sulphate. Heat the liquid to about 85° C. (185° F.), and add the remainder of the sulphuric acid, and water sufficient to just redissolve any crystals of chromic acid that may have been formed. Allow to cool, collect and drain the crystals, and dry them on porous tiles at a temperature not exceeding 40° C. (104° F.), in an air bath. From the mother liquor more crystals may be obtained by evaporation.



Notes.—The presence of a little sulphuric acid adhering to the crystals cannot be objected to, but the preparation should not contain over 5 per cent. Although always moist, it should not be wet.

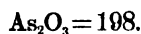
Chromic acid should be preserved in glass stoppered vials.

Description.—Fine red, needle-shaped crystals, which are very deliquescent. They have a strongly corrosive action on organic matter, and decompose such substances as alcohol, sugar or glycerin with explosive violence.

Tests.—Sulphuric acid should be nearly absent. Prove this by dissolving a Gm. or two in cold water, with addition of a little HCl, and adding solution of BaCl₂. Not more than a slight turbidity should appear.

ARSENOUS ANHYDRIDE.**ACIDUM ARSENOSUM.**

[ARSENIOS ACID.]



A heavy, white solid, occurring either as an opaque powder, or in transparent or semi-transparent masses, which usually have a striated appearance; permanent in the air, odorless and tasteless, and having a

faintly acid reaction, Soluble in 30 to 80 parts of water at 15° C. (59° F.), the solubility varying with its physical condition.

It dissolves slowly in about 15 parts of boiling water, and is readily soluble in hydrochloric acid, and alkaline solutions, forming, with the latter, arsenites usually of the type K_2HAsO_3 , on which basis the figures in the table below are calculated.

Recently sublimed arsenous oxide is transparent, having the appearance of glass; but by keeping it becomes opaque, this change beginning at the surface and gradually extending toward the center of the mass until the whole is opaque like porcelain.

A solution of opaque arsenous oxide made with boiling water contains over 10 per cent., but on cooling only 2.9 per cent. of the arsenic remains in the solution.

Its solution in glycerin undergoes some chemical change not yet fully explained.

Arsenous oxide may be reduced to fine powder by sufficient trituration in a wedgewood mortar, keeping the contents moist with alcohol to prevent the poisonous dust from rising.

Tests.—See the method under Volumetric Analysis, by use of iodine solution. The oxide is dissolved in water to which some sodium bicarbonate has been added. The titration is then performed in the usual way.

Composition.—Arsenous oxide, erroneously called arsenous acid, is composed of 75.76 per cent. As and 24.24 per cent. O. When dissolved in water it yields true arsenous acid, as follows: $As_2O_3 + 3H_2O = 2H_3AsO_3$. The molecular weight of arsenous acid is 126, and 100 parts of arsenous oxide yield 127.8 parts of arsenous acid.

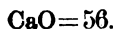
Saturating power.—100 parts of arsenous oxide will form arsenites with the alkalis, requiring of each the following amounts:

Potassium carbonate 139.39 parts.....	} Yielding 204.04 parts of potassium arsenite.
Potassium bicarbonate, 202.00 parts.....	
Solution of potassa (5 per cent.), 2262.6 parts..	
Sodium carbonate 107.07 parts.....	} Yielding 171.71 parts of sodium arsenite.
Sodium bicarbonate 169.69 parts.....	
Solution of soda (5 per cent.), 1616 parts.....	
Ammonia water (10 per cent.), 343.43 parts ...	} Yielding 161.61 parts of ammonium arsenite.
Ammonium carbonate, 96.66 parts.....	

CALCIUM OXIDE.

CALCI OXIDUM.

[CALX. LIME.]



Fill a Hessian crucible with fragments of marble, and heat strongly in a furnace until the carbon dioxide is expelled.

Notes.—Good lime, consisting of calcium oxide free from carbonate, is not easily to be found in commerce. That made in lime kilns varies greatly in quality and purity. For chemical and pharmaceutical purposes a good white lime, free from other earth metals as well as from calcium carbonate, is required. The assay processes for opium and cinchona call for its use. When good pieces cannot be selected from commercial quick-lime, it may be made without difficulty by calcining marble as suggested.

Description.—When made from lime-stone it has usually a gray tinge, but when marble is employed it should be pure white.

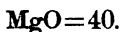
Tests.—The pieces should slake immediately when cold water is poured over them, and the slaked lime so obtained should dissolve completely in hydrochloric acid. This solution should not show more than slight turbidity when neutralized with ammonia water or when precipitated by barium chloride solution.

The solution in hydrochloric acid when neutralized by ammonia should be completely precipitated by solution of ammonium carbonate, which can be shown by filtering, evaporating the filtrate to dryness and strongly igniting. Not more than a trace of residue should be left.

LIGHT MAGNESIUM OXIDE.

MAGNESII OXIDUM LEVE.

[MAGNESIA LEVIS. LIGHT MAGNESIA.]



Light magnesium carbonate, any convenient quantity.

Rub the magnesium carbonate through a No. 60 sieve; then heat it in a capacious unglazed earthenware dish with constant stirring, on a sand-bath, until a sample removed from the center, cooled, mixed with a little water, and then dropped into diluted sulphuric acid, gives but a very slight effervescence.

One Gm. of the product, thoroughly mixed with 15 C.c. of water in a beaker, after standing one hour, forms a gelatinous mass sufficiently firm to remain in the beaker when the latter is inverted. Keep it in a tightly corked bottle.

Reaction.— $4(\text{MgCO}_3) \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O} = 5\text{MgO} + 4\text{CO}_2 + 6\text{H}_2\text{O}.$

Notes.—If heated until all traces of carbon dioxide have been expelled, the product does not become hydrated and form a gelatinous mass when mixed with water. Considerable effervescence with acids should, however, not be allowed. When the process of calcination is not continued sufficiently long an anhydrous basic carbonate is formed which gelatinizes with water but does not retain this property.

Light magnesia must be kept in small bottles tightly corked, the corks to be dipped in melted paraffin to effectually exclude air. The preparation rapidly takes up carbonic acid unless thoroughly protected.

Description.—A white very fine light powder, nearly insoluble in water and quite insoluble in alcohol.

Tests.—Should effervesce but very slightly when mixed with water and then treated with dilute acid.

A solution in nitric acid should be clear and should give no precipitate with barium nitrate or silver solution, showing absence of sulphates and chlorides. A solution in hydrochloric acid treated with an excess of ammonium chloride, then made alkaline with ammonium hydrate, and finally treated with ammonium carbonate, should remain clear, showing absence of compounds of iron, aluminium and calcium.

Saturating power.—100 parts of magnesia will saturate:

Diluted sulphuric acid (10 per cent. H_2SO_4) 2450 parts.

Acetic acid (98 per cent. $HC_2H_3O_2$), 833.8 parts.

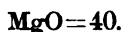
Citric acid (100 per cent. $H_3C_6H_5O_7 \cdot H_2O$), 350 parts.

Tartaric acid (100 per cent. $H_2C_4H_4O_6$), 375 parts.

HEAVY MAGNESIUM OXIDE. -

MAGNESII OXIDUM PONDEROSUM.

[MAGNESIA PONDEROSA. HEAVY MAGNESIA.]



Heavy magnesium carbonate, any desired quantity.

Put it in a Cornish or Hessian crucible closed loosely by a cover and expose it to a low red heat until a small quantity, taken from the center of the crucible, cooled, mixed with a little water, and dropped into diluted sulphuric acid, causes no effervescence.

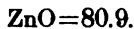
Reaction.— $4(MgCO_3) \cdot Mg(OH)_2 \cdot 5H_2O = 5MgO + 4CO_2 + 6H_2O$.

Description.—A white powder differing from the preceding chiefly in density. As the heavy magnesia does not form a gelatinous mass with water, the official description is in that respect erroneous.

Tests.—As for light magnesia.

ZINC OXIDE.

ZINCI OXIDUM.



Precipitated zinc carbonate, any desired quantity.

Heat it at a low red heat until the water and carbonic oxide are wholly expelled.

Reaction— $2(ZnCO_3) \cdot 3Zn(OH)_2 = 5ZnO + 2CO_2 + 3H_2O$.

Zinc oxide is also made by heating the metal in free access of air. This is now the principal method employed on a large scale, and yields a good product. The zinc oxide thus obtained by oxidation and sublimation is sometimes called "flowers of zinc."

Notes.—A pure white zinc oxide is required for pharmaceutical purposes, and hence the precipitated carbonate used for its preparation must also be pure. The carbonic oxide and water are easily expelled (already at 250° C.). Too high heat gives the product a yellow color, which it retains for a long time, whitening again only gradually by the influence of sun-light. A too high heat also makes the product feel harsh. Only a small quantity should be calcined at one time.

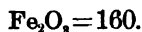
Description.—A soft flaky impalpable powder having specific gravity of 5.6.

Tests. Should turn yellow when heated in a test tube, and become white again on cooling. It should be insoluble in water and completely soluble in dilute acids. The solution in dilute nitric acid should give no test for chlorides or sulphates, while the solution in hydrochloric acid should give no indication of presence of lead or iron.

FERRIC OXIDE.

FERRI OXIDUM.

[SESQUIOXIDE OF IRON.]



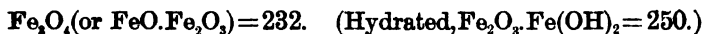
May be obtained by simply igniting ferric hydrate, when a shining dark brown granular ferric oxide remains, which becomes reddish brown when powdered.

“Jewelers’ Crocus” is a finely divided ferric oxide obtained by igniting iron oxalate in an iron dish until it ceases to lose weight and a uniform fine brown powder remains.

The formerly official preparation called “subcarbonate of iron,” which is still considerably used, also consists almost entirely of ferric oxide.

MAGNETIC OXIDE OF IRON.

FERRI OXIDUM NIGRUM.



Solution of tersulphate of iron 230 C.c.

Ferrous sulphate 60 Gm.

Ammonia water 500 C.c.

Water, sufficient.

Dissolve the ferrous sulphate in 2,000 C.c. of water and filter; add the solution of ferric sulphate; then pour this liquid gradually and with constant stirring into the ammonia water previously diluted with 1,000 C.c. of water. Boil the mixture fifteen minutes. Wash the precipitate, first by decantation and afterwards on a filter until the washings cease to give a precipitate with test-solution of barium chloride. Then dry the product.

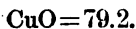


Notes.—The boiling is directed for the purpose of decomposing the hydrated oxides precipitated by the ammonia, expelling the water of hydration. The product then keeps well, not becoming oxidized into ferric oxide as readily as it would otherwise do.

Description.—A perfectly black, impalpable, tasteless, inodorous and insoluble powder.

CUPRIC OXIDE.

CUPRI OXIDUM.



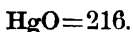
This oxide is prepared as a fine black powder or as small granules, most readily by ignition of the nitrate.

It is used in organic analysis as an oxidizing agent.

RED OXIDE OF MERCURY.

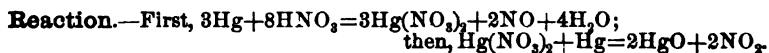
HYDRARGYRI OXIDUM RUBRUM.

[RED PRECIPITATE.]



Mercury	320 Gm.
Nitric acid	1,800 C.c.

Dissolve 160 Gm. of the mercury in the acid previously diluted with 800 C.c. of water. Evaporate the solution to dryness. To the residue add the remainder of the mercury, and triturate until all globules of mercury disappear and a uniform mixture results. Heat this in a porcelain dish on a sand-bath, stirring frequently, until acid vapors cease to be evolved.



Notes.—The nitrate is decomposed by heat, red fumes (nitrogen tetroxide) being evolved. When all the nitrate has been thus decomposed, the acid vapors cease, and the residue is mercuric oxide. Care must be taken to continue the heating until not a trace of nitrate remains. Mercuric oxide when strongly heated becomes very dark, but the red color returns on cooling. If the heat is too high (over $360^\circ \text{C}.$) the oxide decomposes into its elements, which may be discovered by holding a piece of filter-paper over the heated mass, when metallic mercury will condense on the paper.

It is sometimes directed to digest the residue after cooling, with distilled water to which a little solution of soda has been added, the object being to remove

any remaining nitrate. In this case the oxide must afterwards be thoroughly washed, and dried at a gentle heat.

Red oxide of mercury should be reduced to extremely fine powder by trituration before being used.

Description.—When prepared on a large scale the red oxide of mercury consists of shining crystalline scales of a dark orange red color. Prepared in smaller lots, it is a brick-red powder. When trituated it becomes lighter in color, and more yellow the finer its division. It is permanent in the air, inodorous and tasteless, insoluble in water or alcohol, but wholly soluble in nitric or hydrochloric acid. Heated to a high temperature it first darkens; when the heat is further increased the mercuric oxide decomposes, giving off oxygen and separating metallic mercury, and is finally volatilized without residue. When digested on a water-bath, with a strong solution of oxalic acid, it does not change color within two hours (difference from yellow mercuric oxide).

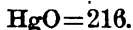
Tests.—Should be completely insoluble in water, but should dissolve to a clear solution in nitric acid.

The dry substance, when heated, should give off no red fumes, showing absence of undecomposed nitrate.

YELLOW MERCURIC OXIDE.

HYDRARGYRI OXIDUM FLAVUM.

[PRECIPITATED OXIDE OF MERCURY.]



Corrosive mercuric chloride, in powder. 100 Gm.

Solution of potassa. 900 C.c.

Water, sufficient.

Dissolve the mercuric chloride in 5,000 C.c. of hot water, and filter. Pour the filtrate, when cold, into the solution of potassa previously diluted with one liter of water, stirring constantly. Set the liquid containing the precipitate aside for twenty-four hours. Then decant the supernatant liquid from the precipitate, and wash the latter repeatedly by the affusion and decantation of distilled water. Continue the washing on a filter until the washings cease to be affected by test solution of nitrate of silver. Let the precipitate drain, and dry it, between bibulous paper, in a dark place, at a temperature not exceeding 40° C. (104° F.).

Keep the product in well stoppered bottles, protected from light.



Notes.—The mercuric chloride is to be used in powder, and the water in which it is dissolved must be hot, in order to save time; but the solution must be allowed to become cold before it is added to the solution of potassa. Very hot solutions would yield a product consisting partly of red oxide, and even the drying of freshly precipitated yellow mercuric oxide by the aid of heat renders it reddish and affords a preparation which does not withstand the oxalic acid test. To avoid the formation of any of the red variety of the oxide, and thus obtain a light yellow product, therefore requires the use of cold solutions.

The solutions must also be comparatively dilute, for if strong solutions are employed the product is liable to be contaminated by oxychlorides of mercury, one of which is nearly black ($\text{HgCl}_2 \cdot 2\text{HgO}$), and another brick-red ($\text{HgCl}_2 \cdot 8\text{HgO}$). These oxychlorides, or either of them, may also be formed if the mercuric chloride is allowed to be present in excess over the potassa; which happens when the solution of potassa is poured into the solution of mercuric chloride, and may also

result from a failure to stir the solution of potassa briskly in the act of pouring the mercury solution into it, or from adding the mercury salt too rapidly.

If the potassa used contains carbonate, the precipitate will contain dark brown mercuric carbonate, which usually falls after the oxide has subsided, and thus forms a thin film over the precipitate.

Both the oxychlorides and the carbonate can be broken up by digestion or even maceration with an excess of potassa; but this requires time, and results in waste of materials. Their formation is readily prevented by the use of proper materials and a strict observance of the directions given in the working formula.

The precipitate is to be washed until the washings, slightly acidulated with nitric acid, no longer give a reaction for chlorine, with test solution of silver nitrate.

Light reduces precipitated mercuric oxide, causing the separation of finely divided metallic mercury, which darkens the product. Hence the precipitate should be prepared, washed and dried with as little exposure to light as possible.

Yellow oxide of mercury can also be made from mercuric nitrate, and soda may be used in place of potassa.

Description.—A heavy yellow powder, which becomes red on application of strong heat. Insoluble in water, but soluble in nitric and hydrochloric acid.

Tests.—Heated with strong solution of oxalic acid, it forms mercuric oxalate readily, and in this respect differs from the red oxide.

YELLOW WASH.

LOTIO FLAVA.

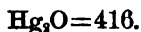
Mercuric chloride..... 1 Gm.
Lime water.....250 C.c.

Triturate the mercuric chloride to fine powder, add the lime water, gradually continuing the trituration.

Notes.—Yellow mercuric oxide is formed, which settles to the bottom. The preparation must, therefore, be vigorously shaken each time it is to be used.

MERCUROUS OXIDE.

HYDRARGYRI OXIDUM NIGRUM.



Prepared by macerating freshly precipitated mercurous chloride with solution of potassa in excess. The thoroughly washed and still moist mercurous chloride is gradually added to the solution of potassa, with diligent stirring; the whole is well shaken, and then set aside in a dark place until the black mercurous oxide has settled. This is then washed with cold distilled water, collected, and dried between folds of blotting paper in a cool, dark place.

Must be kept well protected from the light.

About 12 parts of precipitated calomel, and 24 parts of solution of potassa of 1.33 specific gravity, will be required to prepare 10 parts of mercurous oxide.

Description.—A greenish black, heavy, inodorous, tasteless powder, insoluble in water or alcohol. Readily and completely soluble in warm nitric acid. Hydrochloric acid converts it into white mercurous chloride. Volatilizes without residue.

BLACK WASH.

LOTIO NIGRA.

Calomel.....	1 Gm.
Lime water.....	150 C.c.

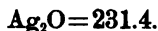
Triturate the calomel with the lime water gradually added.

Notes.—Black mercurous oxide is formed, which is heavy and insoluble in the liquid. The preparation is therefore to be thoroughly shaken each time it is to be used.

To throw the calomel into a bottle and shake it with the lime water is inadmissible, as little lumps are then formed which protect a portion of the calomel in the interior from the action of the calcium hydrate. A good preparation cannot be obtained unless the powder is triturated with the lime water.

SILVER OXIDE.

ARGENTI OXIDUM.



Silver nitrate.....	100 Gm.
Distilled water.....	200 C.c.
Solution of potassa.....	600 C.c.

Dissolve the silver nitrate in the water. To this solution add solution of potassa so long as any precipitate is produced by it. Wash the precipitate with distilled water until the washings are nearly tasteless. Dry the product and keep it well protected from the light.

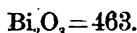
Reaction.— $2\text{AgNO}_3 + 2\text{KOH} = \text{Ag}_2\text{O} + 2\text{KNO}_3 + \text{H}_2\text{O}$.

Notes.—Silver oxide easily parts with its oxygen, and hence must not be brought in contact with readily oxidizable substances, as explosion may result. Moderate heat also decomposes it. With ammonia it forms a violently explosive compound known as "fulminate of silver." Great care is accordingly necessary in handling this preparation. It should be kept in a well-closed bottle and in a cool place, and it is not safe to keep pills made with silver oxide and solid extracts any length of time. The best excipient for such pills is perhaps kaolin ointment.

Description.—A dark brown powder soluble in about 8,000 parts of water, to which it imparts an alkaline taste; on application of strong heat it loses all oxygen, leaving metallic silver.

Tests.—Completely soluble in nitric acid. From this solution chlorides throw down silver chloride.

It is capable of forming the same chloride when shaken with solutions of metallic chlorides, as of NaCl.

BISMUTHOUS OXIDE.**BISMUTHI OXIDUM.**

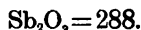
Subnitrate of bismuth	1 part.
Solution of soda	4 parts.

Mix and boil for five minutes; set it aside to cool and settle; decant the supernatant liquid; wash the precipitate thoroughly with distilled water, and dry by water-bath heat.

Reaction.— $2\text{BiONO}_3 \cdot \text{H}_2\text{O} + 2\text{NaOH} = \text{Bi}_2\text{O}_3 + 2\text{NaNO}_3 + 2\text{H}_2\text{O}$.

Description.—Bismuth oxide is a fine, soft powder, having a greenish yellow tint, so pale as to be nearly white. It is inodorous, tasteless, and insoluble in water.

Tests.—It is soluble in nitric acid, and from this solution precipitate the white hydrated nitrate (subnitrate) by addition of water.

ANTIMONIOUS OXIDE.**ANTIMONII OXIDUM.**

Solution of chloride of antimony	400 C.c.
Sodium carbonate	150 Gm.
Water, sufficient.	

Pour the solution of chloride of antimony into 8,000 C.c. of warm water, stirring well; let the precipitate subside, draw off the supernatant liquid by a siphon, add 4,000 C.c. of warm water, stir well, let settle, and again siphon off the wash water; repeat this a third time. Now add the sodium carbonate previously dissolved in 1,000 C.c. of water, let the mixture stand for half an hour, stirring frequently, and then collect the oxide on a filter and wash it with boiling water until the washings cease to give a precipitate with test solution of silver nitrate acidulated with nitric acid. Lastly, dry the product at not above 100° C. (212° F.).

Reaction.— $12\text{SbCl}_3 + 15\text{H}_2\text{O} = 2\text{SbCl}_5 + 5\text{Sb}_2\text{O}_3 + 30\text{HCl}$; and subsequently, $2\text{SbCl}_5 + 5\text{Sb}_2\text{O}_3 + 3\text{Na}_2\text{CO}_3 = 6\text{Sb}_2\text{O}_3 + 6\text{NaCl} + 3\text{CO}_2$.

Notes.—The object of using *warm* water in precipitating the oxychloride of antimony, and in washing it, is to remove as much as possible of the lead chloride that may contaminate the precipitate in case the solution of chloride of antimony contained that impurity. To convert the oxychloride into oxide, ammonia can be used instead of sodium carbonate.

Description.—A white, crystalline powder, insoluble in water, inodorous, and tasteless. When heated it turns yellow, but becomes white again on cooling.

Tests.—The proper reagents should show absence of chlorides, sulphates and metallic impurities. It should be soluble in boiling solution of potassium acid tartrate.

HYDRATES.

The hydrates of potassium, sodium, and ammonium (ammonia water) are frequently used in pharmaceutical chemistry as precipitants and for other purposes. The potassium and sodium hydrates are prepared from the carbonates from which the carbonic acid is removed by precipitation with calcium hydrate.

Calcium and barium hydrates are employed for similar purposes, to liberate alkaloids, etc. These are made by adding water to the oxides.

Aluminium hydrate and ferric hydrate are insoluble, and are made by precipitation.

POTASSIUM HYDRATE.

POTASSA.

[CAUSTIC POTASH.]

KOH = 56.

When impure potassa is dissolved in alcohol, any carbonate, sulphate, and the greater portion of any chloride present remain undissolved, and may thus be removed. The alcohol may then be distilled off from the clear, decanted solution, and the remaining potassa is dried and fused in a silver capsule. Although the solution is brown from the action of the alkali upon the organic substances in the alcohol, the fused potassa will still be white. To prevent the formation of carbonate, a little boiled distilled water is added from time to time to the alcoholic solution during its evaporation.

It should be quite white, hard, crystalline in the fracture, and dry.

Potassa must be kept in bottles of hard glass, as it attacks soft glass. Green glass free from lead is best. Glass stoppers in bottles containing potassa or its solution, are acted upon by the alkali, and often become so firmly fastened to the neck that they cannot be removed. To prevent this a little petrolatum may be rubbed upon the stopper before inserting it. This also effectually excludes air, and thus protects the potassa from moisture and carbonic acid.

Description.—It is usually sold for chemical and pharmaceutical purposes in fused sticks. It also appears in large crystalline masses. It is white and very deliquescent, caustic, acid and corrosive.

Tests.—Pure KOH is quickly soluble in water, and should give no effervescence with acids. Under the subject of Volumetric Analysis will be found the method of quantitative testing.

Saturating power.—100 parts of KOH will saturate:

Acetic acid (36 per cent. $\text{HC}_2\text{H}_3\text{O}_2$), 297.6 parts.

Acetic acid, diluted (6 per cent. $\text{HC}_2\text{H}_3\text{O}_2$), 1,785.8 parts.

Acetic acid, glacial (99 per cent. $\text{HC}_2\text{H}_3\text{O}_2$), 108.2 parts.

Arsenous oxide (100 per cent. As_2O_3), 88.4 parts.
 Benzoic acid (100 per cent. $\text{HC}_7\text{H}_5\text{O}_2$), 217.8 parts.
 Citric acid (100 per cent. $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$), 125 parts.
 Hydrobromic acid (84 per cent. HBr), 424.3 parts.
 Hydrobromic acid, diluted (10 per cent. HBr), 1442.8 parts.
 Hydrochloric acid (31.9 per cent. HCl), 203.8 parts.
 Hydrochloric acid, diluted (10 per cent. HCl), 650 parts.
 Hydrocyanic acid, diluted (2 per cent. HCy), 2410.7 parts.
 Lactic acid (75 per cent. $\text{HC}_3\text{H}_5\text{O}_3$), 214.2 parts.
 Nitric acid (69.4 per cent. HNO_3), 162.1 parts.
 Nitric acid, diluted (10 per cent. HNO_3), 1125 parts.
 Oleic acid (100 per cent. $\text{HC}_{18}\text{H}_{33}\text{O}_2$), 503.6 parts.
 Phosphoric acid (50 per cent. H_3PO_4), 175 parts.
 Phosphoric acid, diluted (10 per cent. H_3PO_4), 875 parts.
 Salicylic acid (100 per cent. $\text{HC}_7\text{H}_5\text{O}_3$), 246.4 parts.
 Sulphuric acid (100 per cent. H_2SO_4), 87.5 parts.
 Sulphuric acid (96 per cent. H_2SO_4), 91.1 parts.
 Sulphuric acid, diluted (9.6 per cent. H_2SO_4), 911 parts.
 Tartaric acid (100 per cent. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$), 133.9 parts.

As compared with other potassium compounds, 100 parts of KOH equals 178.6 parts of potassium bicarbonate, or 147.3 parts of potassium carbonate (100 per cent. $2\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$).

As compared with sodium compounds, 100 parts of KOH equals 71.43 parts of NaOH , 150 parts of sodium bicarbonate (100 per cent. NaHCO_3), or 255.36 parts of sodium carbonate (100 per cent. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$).

As compared with the corresponding ammonium compounds, 100 parts of KOH equals 80.357 parts of NH_3 , 303.57 parts of official ammonia water (10 per cent. NH_3), 103.41 parts of stronger ammonia water (28 per cent. NH_3), or 93.45 parts of ammonium carbonate.

POTASSA WITH LIME.

POTASSA CUM CALCE.

Potassa	1 part.
Lime	1 part.

Rub them together so as to form a powder, and keep it in a well stoppered bottle.

Notes.—A warm mortar should be used. The mixture is less corrosive than pure potassa. The lime, however, keeps the potassa free from carbonate. It should be kept either in glass stoppered bottles, the stoppers to be rubbed over with petrolatum, or in corked bottles, the corks to be thoroughly paraffined.

Description.—A grayish-white powder, deliquescent, having a strongly alkaline reaction, and responding to the tests for calcium and potassium. It should be soluble in hydrochloric acid without leaving more than a small residue.

SOLUTION OF POTASSA.

LIQUOR POTASSÆ

An aqueous solution of hydrate of potassium (KOH, 56.), containing about 5 per cent. of the hydrate.

Bicarbonate of potassium.....	90 Gm.
Lime.....	40 Gm.
Distilled water, sufficient.	

Dissolve the bicarbonate of potassium in 400 C.c. of distilled water, heat the solution until effervescence ceases, and then raise it to boiling. Slake the lime and make it into a smooth mixture with 400 C.c. of distilled water, and heat it to boiling. Then gradually add the first liquid to the second and continue the boiling for ten minutes. Remove the heat, cover the vessel tightly, and, when the contents are cold, add enough distilled water to make the whole weigh 1,000 Gm. Lastly, strain through linen, or remove the clear solution, after subsidence of the precipitate, by means of a siphon.

Solution of potassa should be kept in well stoppered bottles.

Reaction.—The potassium bicarbonate is first converted into normal carbonate by boiling the solution. Then, $K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3$.

Notes.—The potassium bicarbonate is used in preference to monocarbonate, because bicarbonate is readily obtained nearly pure, whereas carbonate usually contains various impurities. The lime is used in considerable excess, but no lime will be contained in the finished solution of potassa, as calcium hydrate is insoluble in that liquid. Theoretically 1 part of lime is sufficient to causticize 8.6 parts of potassium bicarbonate when the process is conducted as prescribed in the official process, which is the one given above. It would be a decided improvement upon this process to first wash the calcium hydrate, throwing away the first portion of water used as in the process for making lime water; this removes dust, salts, etc. An unnecessarily large excess of lime is disadvantageous in that the calcium hydrate settles more slowly than the carbonate.

Potassium carbonate may be causticized by calcium hydrate without the aid of heat, but the calcium carbonate then formed is very light, settles slowly, and retains much liquid. By using hot solutions, as directed by the Pharmacopœia, a much more dense calcium carbonate is formed which settles rapidly, so that the solution can be separated with less waste.

Not less than 8 parts, and preferably 12 parts of water should be taken for each part of normal potassium carbonate used. The process of the U. S. Pharmacopœia employs about $10\frac{1}{2}$ parts, for 90 parts of bicarbonate corresponds to about 77 parts of monocarbonate, and the water used is 800 parts. If a more concentrated solution is used the decomposition will be incomplete. The reaction is complete when the liquid no longer effervesces with dilute acid, and does not cause a turbidness when dropped into clear lime water.

Solution of potassa can well be evaporated in an iron pot down to about 1.16 specific gravity without danger of attacking the iron. A stronger solution, however, would attack the metal. In any event a solution of potassa should not be allowed to remain long in contact with iron, and whenever such a solution is to be concentrated in an iron vessel, the evaporation should be hastened as much as possible.

Straining or filtering the solution is liable to discolor it. A better plan is to let it stand long enough to settle thoroughly, and then to separate the clear solution by means of a siphon. In cases where filtration seems unavoidable, the most appropriate filtering medium is coarsely powdered and washed marble.

The Pharmacopœia gives the following alternate process for making this solution:

Potassa 56 Gm.
 Distilled water..... 944 C.c.
 Dissolve.

An excess of potassa is here used to compensate for moisture, carbonate, and other impurities contained in it.

Description.—A clear, colorless solution of an acrid, caustic taste. Sp. gr. 1.086; sp. vol. 0.965.

Tests.—It should not effervesce with acids, and when a drop on a platinum loop is held in the Bunsen flame only a violet color should be produced.

The solution neutralized by nitric acid should not be precipitated by barium nitrate or silver nitrate.

56 Gm. of the solution should require for neutralization 50 C.c. of normal hydrochloric acid.

Strength.—The various official solutions of potassa compare as follows:

Pharmacopœia.	Per cent. KOH.	Specific gravity, 15° C. Water at 4° C.—1.000.	Number of parts representing 56 parts of KOH.
Germany (1872).....	32.50	1.330	167.44
Sweden (1869).....	20	1.196	280
Germany (1882).....	15	1.150	337.33
Great Britain (1885).....	5.84	1.058	958.83
United States (1882).....	5	1.086	1120

Specific Gravity and Percentage Strength of Solutions of KOH.

(Tünnermann and Schiff.)

Per cent. of KOH.	Sp. gr. 15°.
1	1.009
5	1.041
10	1.083
15	1.128
20	1.177
25	1.230
30	1.288
35	1.349
40	1.411
45	1.475
50	1.538
55	1.604
60	1.667
65	1.729
70	1.790

SODIUM HYDRATE.**SODA.**

[CAUSTIC SODA.]

 $\text{NaOH} = 40.$

Prepared from sodium carbonate by double decomposition with calcium hydrate in the same manner as potassium hydrate is prepared from potassium carbonate. Pure sodium hydrate is soluble in alcohol, but the carbonate is insoluble in it; hence impure sodium hydrate is purified by solution in alcohol and subsequent distillation as described under Potassa.

Soda is to be preserved in the same manner as potassa.

Description.—It is less corrosive than potassa. A white, hard, opaque solid, generally in form of irregular masses, deliquescent in moist air, but effervescent in dry air. Soluble in about its own weight of water, and very soluble also in alcohol.

Tests.—Should be soluble in water and alcohol, and give no effervescence with acids.

The amount of pure NaOH is found by means of standard acid solution given under Volumetric Analysis.

Saturating power.—100 parts of NaOH will saturate:

- Acetic acid (86 per cent. $\text{HC}_2\text{H}_3\text{O}_2$), 416.6 parts.
- Acetic acid, diluted (6 per cent. $\text{HC}_2\text{H}_3\text{O}_2$), 2,500 parts.
- Acetic acid, glacial (99 per cent. $\text{HC}_2\text{H}_3\text{O}_2$), 151.6 parts.
- Arsenous oxide (100 per cent. As_2O_3), 123.7 parts.
- Benzoic acid (100 per cent. $\text{HC}_7\text{H}_5\text{O}_2$), 305 parts.
- Citric acid (100 per cent. $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$), 175 parts.
- Hydrobromic acid (34 per cent. HBr), 593.7 parts.
- Hydrobromic acid, diluted (10 per cent. HBr), 2020 parts.
- Hydrochloric acid (31.9 per cent. HCl), 235.2 parts.
- Hydrochloric acid, diluted (10 per cent. HCl), 910 parts.
- Hydrocyanic acid, diluted (2 per cent. HCy), 3,375 parts.
- Lactic acid (75 per cent. $\text{HC}_3\text{H}_5\text{O}_3$), 300 parts.
- Nitric acid (69.4 per cent. HNO_3), 227 parts.
- Nitric acid, diluted (10 per cent. HNO_3), 1,575 parts.
- Oleic acid (100 per cent. $\text{HC}_{18}\text{H}_{33}\text{O}_2$), 705 parts.
- Phosphoric acid (50 per cent. H_3PO_4), 245 parts.
- Phosphoric acid, diluted (10 per cent. H_3PO_4), 1,325 parts.
- Salicylic acid (100 per cent. $\text{HC}_7\text{H}_5\text{O}_3$), 345 parts.
- Sulphuric acid (100 per cent. H_2SO_4), 123.5 parts.
- Sulphuric acid (96 per cent. H_2SO_4), 127.6 parts.
- Sulphuric acid, diluted (9.6 per cent. H_2SO_4), 1,276 parts.
- Tartaric acid (100 per cent. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$), 187.5 parts.
- Valeric acid (100 per cent. $\text{HC}_5\text{H}_9\text{O}_2$), 255 parts.

As compared with other sodium compounds, 100 parts of NaOH equals 210 parts of sodium bicarbonate (100 per cent. NaHCO_3), or 357.5 parts of sodium carbonate (100 per cent. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$).

As compared with potassium compounds, 100 parts of NaOH equals 140 parts of KOH, 250 parts of potassium bicarbonate, or 206.25 parts of potassium carbonate (100 per cent. $2\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$).

As compared with ammonium compounds, 100 parts of NaOH equals 42.5 parts of NH_3 , 425 parts of official ammonia water (10 per cent. NH_3), 151.8 parts of stronger ammonia water (28 per cent. NH_3), or 180.83 parts of ammonium carbonate.

SOLUTION OF SODA.

LIQUOR SODÆ.

An aqueous solution of hydrate of sodium (NaOH, 40.), containing 5 per cent. of the hydrate.

Carbonate of sodium.....180 Gm.

Lime..... 80 Gm.

Distilled water, sufficient.

Dissolve the carbonate of sodium in 400 C.c. of boiling distilled water. Slake the lime and make it into a smooth mixture with 400 C.c. of distilled water, and heat to boiling. Then gradually add the first liquid to the second, and continue the boiling for ten minutes. Remove the heat, cover the vessel tightly, and, when the contents are cold, add enough distilled water to make the whole mixture weigh 1,000 Gm. Lastly, strain through linen, or remove the clear solution, after subsidence of the precipitate, by means of a siphon.

Solution of soda should be kept in well stoppered bottles.

Reaction.— $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 = 2\text{NaOH} + \text{CaCO}_3$.

Notes.—The general observations given under Solution of Potassa apply also to the preparation of solution of soda. This solution has the sp. gr. 1.059, and the sp. vol. 0.944.

Specific Gravity and Percentage Strength of Solutions of NaOH.

(Schiff).

Per cent. of NaOH.		Sp. gr. 15°.
1	-----	1.012
5	-----	1.059
10	-----	1.115
15	-----	1.170
20	-----	1.225
25	-----	1.279
30	-----	1.332

Per cent. of NaOH.		Sp. gr. 15°.
35	-----	1.384
40	-----	1.437
45	-----	1.488
50	-----	1.540
55	-----	1.591
60	-----	1.643

AMMONIA.**AMMONIA.**

$\text{NH}_3 = 17.$

An experiment illustrating the preparation and properties of this gas has already been given.

AMMONIA WATER.**AQUA AMMONIÆ.**

An aqueous solution containing 10 per cent. of NH_3 . It may be regarded as a solution of ammonium hydrate, NH_4OH .

Best made by mixing 100 weight units of stronger ammonia water (28 per cent. NH_3) with 180 weight units of distilled water, or 112 volume units of stronger ammonia water with 180 volume units of distilled water.

This is what manufacturers call "U. S. P. water of ammonia," having 0.959 specific gravity at 15° C. (59° F.) compared with water at 4° C. as unit, and corresponding to 16° Beaumé. Its sp. vol. is 1.043.

Description.—A colorless solution lighter than water, and possessing the characteristic odor of the gas. See also the notes under Stronger Ammonia Water.

Tests.—It should be completely volatile, and when neutralized with nitric acid should give no test for sulphates on addition of barium nitrate, nor for chlorides on addition of silver nitrate.

The percentage strength is found by means of standard acid solution as given under the head of Volumetric Analysis.

STRONGER AMMONIA WATER.**AQUA AMMONIÆ FORTIOR.**

Ammonium chloride, in coarse powder 1,000 Gm.
Lime 1,250 Gm.
Distilled water, water, each sufficient.

Slake the lime with 500 C.c. of water; add the ammonium chloride to 500 C.c. of water; mix the whole well, and immediately introduce the mixture into an iron flask. Connect the flask at once, by means of corks, glass tubes and rubber stoppers, with a Woulfe bottle of the capacity of 500 C.c. Connect this with a second Woulfe bottle of the same size, and this in turn with a receiver of the capacity of two liters, and containing 500 C.c. of distilled water. Connect the receiver with still another bottle containing 200 C.c. of distilled water. The Woulfe bottles are to be empty. The second Woulfe bottle and the receiver must each be provided with a siphon safety tube charged with a very short column of mercury.

The iron flask is placed in a sand-bath, and heat is applied. The receiver is to be cooled by cold water. All joints being tight, the heat is gradually raised and continued until no more gas passes over.

For experimental purposes a glass flask may be used instead of that of iron, but the process cannot then be continued until all the gas has been obtained which the ammonium chloride will yield. This has already been illustrated.

The water is added to the lime and ammonium chloride in order to facilitate the reaction. The calcium hydrate must be allowed to become cool before mixing it with the ammonium chloride.

At the conclusion of the operation there will be considerable quantities of liquid in all four bottles. The Woulfe bottles will contain discolored ammonia solutions; the third bottle or receiver, contains a strong solution of ammonia, which is to be diluted with distilled water until of the required strength; the terminal bottle contains weaker ammonia solution, which may be strengthened by charging it with an additional quantity of gas obtained by heating in a flask the contents of the Woulfe bottles.

If ammonium carbonate is used instead of chloride, less heat will be required, but in that case the gas must be passed through a bottle containing milk of lime to fix the carbonic acid.



Notes.—The “stronger water of ammonia” of the Pharmacopœia contains 28 per cent. of ammonia gas. The sp. gr. is 0.900 at 15° C. (59° F.), corresponding to 26° Beaumé. Its sp. vol. is 1.111.

In order to prevent accidents which may cause serious results the Pharmacopœia directs that stronger ammonia water shall be kept in *strong* glass stoppered bottles, only partially filled, and put in a cool place. If the containers are not sufficiently strong, and are too nearly full and kept in a warm place, they may burst. The gas is extremely caustic and acrid. To inhale or smell ammonia without due caution is attended with danger, and a full container with tightly fitting glass-stopper should never be opened, especially if it is not cool, without turning the face aside from it.

The arbitrary designations F, FF, and FFF, which are still used by some manufacturers, have no uniform significance. Usually the “F” means ordinary official or 10 per cent. solution of ammonia; “FF” refers to a solution containing about 14 per cent. of gas, and having the sp. gr. 0.945 corresponding to 18° Beaumé and “FFF” refers to a solution containing about 17.5 per cent. of gas, and having; the sp. gr. 0.933, corresponding to 20° Beaumé. The official description of stronger ammonia water is as follows:

“A colorless, transparent liquid, of an excessively pungent odor, a very acrid and alkaline taste, and a strongly alkaline reaction. Sp. gr. 0.900 at 15° C. (59° F.).”

“Stronger water of ammonia should be kept in strong glass stoppered bottles not completely filled, in a cool place.”

On a manufacturing scale the water of ammonia is made from ammonium sulphate obtained by treating gas liquor with sulphuric acid. The empyreumatic products which accompany the gas prepared from these materials are removed by passing the gas through tubes containing charcoal.

Tests.—As given above.

Saturating power.—100 parts of gaseous NH_3 will saturate:

- Acetic acid (36 per cent. $\text{HC}_2\text{H}_3\text{O}_2$), 980.8 parts.
- Acetic acid, diluted (6 per cent. $\text{HC}_2\text{H}_3\text{O}_2$), 5,881.8 parts.
- Acetic acid, glacial (99 per cent. $\text{HC}_2\text{H}_3\text{O}_2$), 356.5 parts.
- Arsenous oxide (100 per cent. As_2O_3), 291.2 parts.
- Benzoic acid (100 per cent. $\text{HC}_7\text{H}_5\text{O}_2$), 717.6 parts.
- Citric acid (100 per cent. $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$), 411.8 parts.
- Hydrobromic acid (34 per cent. HBr), 1,397.9 parts.
- Hydrobromic acid, diluted (10 per cent. HBr), 4,752.9 parts.
- Hydrochloric acid (31.9 per cent. HCl), 671.2 parts.
- Hydrochloric acid, diluted (10 per cent. HCl), 2,141.2 parts.
- Lactic acid (75 per cent. $\text{HC}_3\text{H}_5\text{O}_3$), 705.9 parts.
- Nitric acid (69.4 per cent. HNO_3), 584 parts.
- Nitric acid, diluted (10 per cent. HNO_3), 3,705.9 parts.
- Phosphoric acid (50 per cent. H_3PO_4), 576.4 parts.
- Phosphoric acid, diluted 10 per cent. H_3PO_4), 2,882.3 parts.
- Salicylic acid (100 per cent. $\text{HC}_7\text{H}_5\text{O}_3$), 811.8 parts.
- Sulphuric acid (100 per cent. H_2SO_4), 288.23 parts.
- Sulphuric acid (96 per cent. H_2SO_4), 300.8 parts.
- Sulphuric acid, diluted (9.6 per cent. H_2SO_4), 3,003 parts.
- Tartaric acid (100 per cent. $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$), 441.2 parts.
- Valeric acid (100 per cent. $\text{HC}_5\text{H}_9\text{O}_2$), 600 parts.

As compared with other ammonium compounds, 100 parts of NH_3 equals 1,000 parts of ammonia water, 357.14 parts of stronger ammonia water, or 307.6 parts of ammonium carbonate.

As compared with potassium compounds, 100 parts of NH_3 equals 329.4 of potassium hydrate, 588.24 parts of potassium bicarbonate, or 485.3 parts of potassium carbonate.

As compared with sodium compounds, 100 parts of NH_3 equals 235.20 parts of sodium hydrate, 841.2 parts of sodium carbonate, or 494.12 parts of sodium bicarbonate.

Specific Gravity and Percentage Strength of Solutions of NH_3 .

(Otto.)

Per cent. of NH_3 .	Sp. gr. 15°.
5	.9783
6	.9745
7	.9707
8	.9669
9	.9631
10	.9593
11	.9555
12	.9517
15	.9419
20	.9251
25	.9106
30	.8976
35	.8864

SPIRIT OF AMMONIA.

SPIRITUS AMMONIÆ.

An alcoholic solution of ammonia containing 10 per cent. of the gas.

Stronger water of ammonia 500 C.c.

Alcohol 1,000 C.c.

Put the ammonia water into a boiling flask of the capacity of about 1,000 C.c.; connect this with a bottle of 1,500 C.c. capacity to be used as a receiver and containing the alcohol. The bent glass tube connecting the flask and the receiver should be of about 10 millimeters' diameter. Place the receiver in ice-cold water. Fit a thermometer in the flask.

Now heat the flask carefully and gradually, by means of a water bath, up to about 60° C. (140° F.), and maintain this temperature in the bath for ten minutes. Then disconnect the receiver and test the solution of ammonia with volumetric solution of oxalic acid to determine its ammoniacal strength; 50 C.c. of that solution should exactly neutralize 8.5 Gm. of official spirit of ammonia. Having ascertained the quantity of volumetric solution of oxalic acid required to neutralize 8.5 Gm. of the product, adjust the strength accordingly to the required standard.

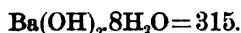
Notes.—The solution obtained is usually stronger than 10 per cent., in which case it simply requires dilution with the proper proportion of alcohol. If the solution be found to contain less than 10 per cent. of NH_3 , the receiver may be

reconnected and the process continued. Should the stronger water of ammonia used fail from any cause to furnish sufficient NH_3 to give the product the requisite strength, put a fresh portion of ammonia water in the flask and repeat the process.

It has the sp. gr. 0.810, and the sp. vol. 1,285.

BARIUM HYDRATE.

BARII HYDRAS.



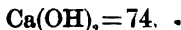
A solution of barium hydrate in water is a valuable laboratory reagent.

It is frequently prepared of a definite strength, and used in volumetric analysis.

CALCIUM HYDRATE.

CALCII HYDRAS.

[SLAKED LIME.]



Lime	16 parts.
Water	10 parts.

Place the lime in a metal pot, pour the water upon it, and when vapor ceases to be disengaged, cover the pot well and set it aside until the contents are cool. Put the slaked lime into an iron-wire sieve, and by gently shaking cause the fine powder to pass through the sieve, rejecting what is left. Put the powder into a bottle and cork tightly.

Notes.—Only recently prepared calcium hydrate is fit to be used for any of the purposes for which slaked lime is prescribed, as it soon becomes contaminated with carbonate. It should be perfectly white.

The water should be added to the lime all at once; otherwise, when too little water is added at first, the hydrate formed will be coarse and hard, and does not afterward disintegrate readily on addition of more water.

The steam disengaged by slaking lime has the odor of hot lye.

It is frequently used as a reagent in chemical analysis, and for many purposes must be free from traces of chlorides, sulphates and alkali metals.

SOLUTION OF LIME.

LIQUOR CALCIS.

[LIME WATER.]

An aqueous solution containing about 0.15 per cent. of hydrate of calcium.

Lime.....	1 part.
Distilled water.....	300 parts.
Water, sufficient.	

Slake the lime by the gradual addition of 6 parts of water, then add 300 parts of water and stir occasionally during half an hour. Allow the mixture to settle, decant the liquid and throw this away. Now add to the residue 300 parts of distilled water, stir well, wait a short time for the coarser particles to subside, and pour the liquid, holding the undissolved lime in suspension, into a glass stoppered bottle. Pour off the clear liquid when wanted for use.

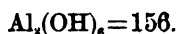
Notes.—The object of rejecting the solution first made is to remove dust and alkalies. After this washing the calcium hydrate furnishes a purer product.

At 19° 5 C. water dissolves about $\frac{1}{317}$ of its weight of calcium hydrate. The excess of hydrate is allowed to remain in the stock bottle in order to keep the solution saturated.

It is clear, colorless, and nearly odorless.

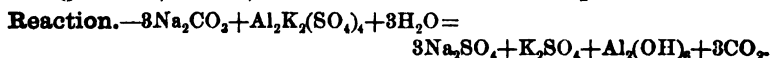
ALUMINIUM HYDRATE.

ALUMINII HYDRAS.



Alum, in powder.....	1 part.
Sodium carbonate.....	1 part.
Distilled water, sufficient.	

Dissolve each salt in 15 parts of distilled water, filter the solutions and heat to boiling. Then having poured the hot solution of carbonate of sodium into a capacious vessel, gradually pour into it the hot solution of alum with constant stirring, and add about 10 parts of boiling distilled water. Let the precipitate subside, decant the clear liquid, and pour upon the precipitate 20 parts of hot distilled water. Again decant, transfer the precipitate to a strainer, and wash it with hot distilled water until the washings give but a faint cloudiness with test-solution of chloride of barium. Then allow it to drain, dry it at a temperature not exceeding 40° C. (104° F.), and reduce it to a uniform powder.



Notes.—In the Pharmacopœial formula the proportions are 11 of alum to 10 of sodium carbonate; this makes the excess of sodium carbonate insufficient.

Theoretically the excess of sodium carbonate in the official proportions is about one-half per cent; but in practice this may be reduced or overcome by impurities present in the salt. At the same time it is necessary to have a decided excess of alkali present throughout the process, and as equal parts of alum and sodium carbonate leave only about ten per cent. excess of the alkali, and as this excess is not too great, these proportions are to be preferred. Unless a sufficient excess of alkali be present from the beginning to the end of the reaction, and the

liquid still remains alkaline after all the alum has been decomposed, the product will contain sulphate. This explains why it is directed that the alum solution must be poured into the alkali solution, and not *vice versa*; it also accounts for the injunction to add the alum solution slowly and with constant stirring.

Aluminium hydrate is a very light, voluminous precipitate, forming an almost gelatinous magma, which settles very slowly if at all, and is therefore difficult to wash. It will of course settle less readily in a dense liquid than in one less dense. Hence the addition of hot water greatly facilitates the washing by decantation. But prolonged contact with boiling water changes the constitution of the hydrate from $\text{Al}_2(\text{OH})_6$ to $\text{Al}_2(\text{OH})_4\text{O}_2$, and the latter compound is insoluble in acids. Hence, the liquid in which the hydrate is suspended must not be boiling, but only hot.

The washed hydrate is to be dried without much heat in order to avoid its becoming hard and gritty.

Aluminium hydrate is chiefly prepared as a preliminary step in the preparation of sulphate, chloride, nitrate, acetate, and other aluminium salts. When prepared for this purpose the hydrate, after having been well washed, is simply drained but not dried before being dissolved in the proper acid.

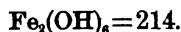
Tests.—It should be soluble in dilute acids. The solution in hydrochloric acid should give no precipitate with barium chloride and no color with potassium ferrocyanide.

The solution obtained by boiling the hydrate with water and filtering should leave no residue on evaporation.

FERRIC HYDRATE.

FERRI OXIDUM HYDRATUM.

[HYDRATED SESQUIOXIDE OF IRON.]



Solution of normal ferric sulphate (500 Gm., or) 380 C.c.

Ammonia water..... (400 Gm., or) 420 C.c.

Water, sufficient.

Dilute the ammonia water with 1,000 C.c. of cold water in the precipitating vessel of about ten liters' capacity. Dilute the solution of ferric sulphate with 5,000 C.c. of cold water, and pour this into the dilute ammonia slowly and during constant stirring. Wash the precipitated ferric hydrate with cold water, first by affusion and decantation, and afterwards on a wetted muslin strainer, until the washings are tasteless. Then let the magma drain, return it to the precipitating vessel, and mix it well with as much cold water as the vessel will hold, or about ten liters. Let settle, decant the supernatant liquid, and again transfer the magma to the wetted strainer and allow it to drain. Continue the washing in this manner until the wash water is no longer affected by test-solution of barium chloride.

[When the ferric hydrate is to be used as an antidote for arsenic, the whole process must be hastened, and the washing need not be carried farther than to remove the mother liquor. To effect this the precipitate is allowed to drain until most of the liquid has run off, and the strainer is then gathered up so as to enclose the magma, which is then forcibly

pressed with the hands until no more liquid can be squeezed out, after which enough water is added to the hydrate to make the weight of the whole product equal to twice the weight of the solution of ferric sulphate used.]



Notes.—*Dilute and cold* solutions are necessary. The diluted solution of ferric sulphate should be poured slowly, or in a small stream, into the diluted ammonia water during constant stirring, as directed. When the whole of the iron solution has been added, the mixture should still have a decidedly ammoniacal odor; as the ammonia gas is diffused through the stratum of air above the surface of the liquid, that air must be fanned or blown away before the odor of the liquid itself can be ascertained.

There are several ferric hydrates, differing from each other in the proportions of water they contain, in color, and in their solubility in acids. The ferric hydrate intended by the Pharmacopœia is $\text{Fe}_2(\text{OH})_6$; another ferric hydrate is $\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2(\text{OH})_6$; and dried ferric hydrate is $\text{Fe}_2\text{O}_3 \cdot (\text{OH})_2$. The more basic it is, and the less water it contains, the less soluble is it. As obtained by the official process, all the necessary precautions being observed, the product is dark reddish brown and readily soluble in citric acid, and in glacial acetic acid. When yellowish brown, brown, grayish brown, or clay-colored, it is basic, insoluble, and unfit for the uses for which it is intended in pharmacy. A light colored ferric hydrate should be at once thrown away.

The solution of ferric sulphate must contain the full amount of ferric sulphate, and be free from ferrous salt in order that the quantity of ferric hydrate obtained from it may be definite; the importance of this will be readily understood from the fact that the proportions of the materials prescribed in several working formulæ for ferric salts are calculated with reference to the amount of ferric hydrate theoretically yielded by the solution of tersulphate of iron.

In summer it is best to use ice for cooling the dilute solutions previous to the precipitation. The chemical reaction generates heat, and if the solutions are already warm the temperature of the mixture is liable to rise sufficiently high to cause the formation of light-colored basic hydrate. But the liquids must not be ice-cold.

Should the quantity of ammonia used be insufficient, or should it be added to the ferric sulphate instead of *vice versa*, basic ferric salts will be formed. A dark red-brown solution containing ferric salt is obtained at first, and no ferric hydrate is thrown down until more ammonia is added.

Ferric hydrate may also be precipitated from ferric chloride or ferric nitrate, and soda may be used as a precipitant instead of ammonia.

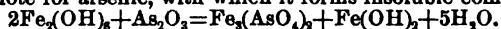
If solution of ferric chloride is used the hydrate formed is more easily washed free from the ammonium salts. If ferric nitrate is used, the product is soluble in an excess of potassium carbonate (Stahl's tincture).

Ferric hydrate precipitated with soda instead of ammonia is much lighter in color and extremely difficult to wash free from sodium salt.

Ferric hydrate forms very soluble compounds with sugar and with glycerin. It is also soluble in solutions of ferric salts, as in solution of ferric chloride. The precipitation of ferric hydrate from solutions of ferric salts by means of alkalies is prevented by the presence of citric acid, tartaric acid, and certain other organic substances.

Description.—When moist it is a dark red-brown magma, insoluble in water, but soluble in citric, tartaric, acetic, hydrochloric, sulphuric, and nitric acids. When dried it is a reddish brown amorphous powder, less readily soluble in acids than the moist hydrate.

Uses.—For the preparation of ferric acetate, citrate, tartrate, nitrate, etc. Also as an antidote for arsenic, with which it forms insoluble compounds:



For whatever purpose it may be required it must be freshly prepared, as it cannot be preserved from decomposition by which basic hydrates are formed, which in no case take the place of the freshly precipitated ferric hydrate.

FERRIC HYDRATE WITH MAGNESIA.**FERRI OXIDUM HYDRATUM CUM MAGNESIA.****[ANTIDOTE FOR ARSENIC.]**

Solution of normal ferric sulphate (65 Gm., or). 50 C.c.

Magnesia..... 10 Gm.

Mix the solution of tersulphate of iron with 130 C.c. of water.

Stir the magnesia with about 150 C.c. of water to a thin milky mixture, transfer this at once to a wide-mouthed bottle of two liters' capacity, and add one liter of water.

The two liquids should be kept in a cool place, and as these materials are intended exclusively for the preparation of an effective antidote for arsenical poisoning, the particular place where they are to be found must be well known by every one concerned.

When the antidote is wanted, the solution of ferric sulphate is at once poured into the magnesia milk, and the mixture thoroughly shaken. It is then ready for immediate use.

The preparation contains ferric hydrate, magnesia, and magnesium sulphate.

DIALYSED SOLUTION OF IRON.**LIQUOR FERRI DIALYSATUS; B.**

Strong solution of ferric chloride, B..... 100 C.c.

Ammonia water..... 175 C.c.

Distilled water, sufficient.

Mix 86 C.c. of the solution of ferric chloride with 600 C.c. of cold distilled water. Pour the mixture slowly and with constant stirring into the ammonia water previously diluted with 400 C.c. of cold distilled water. Wash the precipitate with cold distilled water first by decantation and afterwards on a wetted muslin strainer until the washings cease to be affected by test-solution of silver nitrate acidulated with nitric acid. Let drain, and then press out from the magma as much as possible of the moisture it holds. Add the ferric hydrate to the remainder of the solution of ferric chloride, stir well, and set aside until no more ferric hydrate dissolves. Decant the liquid from the undissolved portion, place it in a covered dialyser, and wash it by dialysis until the washings are nearly tasteless. Then dilute the solution in the dialyser until it measures nearly 400 C.c., and has a sp. gr. of 1.047.

Notes.—When 10 Gm. of this solution is treated with ammonia water in excess, the precipitate, when washed, dried, and ignited, should weigh 0.50 Gm. A drop of the solution, diluted with water, should yield no precipitate with test-solution of silver nitrate acidulated with nitric acid.

This is the so-called "dialysed iron." It will be observed that the product is not the dialysed portion, but the residue after the dialysis. It contains a highly basic ferric oxychloride.

CHAPTER XI.

CHLORIDES.

The chlorides of potassium, sodium, lithium, ammonium, barium, calcium, magnesium and aluminium are readily prepared by saturating hydrochloric acid with the carbonates or hydrates. The chlorides of zinc and iron are made by dissolving the metals in hydrochloric acid. Those of mercury and silver are obtained by double decomposition. All of the chlorides are water-soluble excepting mercurous chloride, and the chlorides of lead and silver.

HYDROCHLORIC ACID.

ACIDUM HYDROCHLORICUM.

[MURIATIC ACID.]

$\text{HCl} = 36.4.$

Preparation.—By double decomposition between common salt (sodium chloride), and sulphuric acid (hydrogen sulphate), yielding hydrochloric acid (hydrogen chloride) and sodium sulphate:



The preparation of this acid as a laboratory experiment has already been given.

Properties.—A colorless, corrosive, fuming liquid, of suffocating odor, and intensely acid taste and reaction. It is a solution of the gaseous hydrogen chloride, and is colorless when pure.

The hydrochloric acid of the Pharmacopœia of the United States contains 31.9 per cent. of absolute hydrochloric acid (HCl), and has the specific gravity 1.16 at 15°C . (59°F .) compared with water at $+4^\circ \text{C}$. (39.2°F .) as 1.000. Its specific volume is 0.862.

At 22° C. (71.6° F.) the official hydrochloric acid has the specific gravity 1.1583 referred to water at the same temperature as unit.

On heating it with black oxide of manganese, an abundance of chlorine gas is given off.

The official acid is what manufacturers call "C. P." The usual half-gallon acid bottle holds 6 lbs. of this acid. Strong hydrochloric acid gives off white vapors, due to the difference in the proportion of moisture contained in the air and in the acid as well as to the formation of ammonium chloride when the hydrogen chloride meets the ammonia of the atmosphere.

Tests.—Volatilizes without residue.

If 1 C.c. of the acid be diluted with water to 10 C.c., and slightly supersaturated with water of ammonia, no precipitate should be formed on gently warming (iron or much lead); the liquid should not have a blue tint (copper), and the further addition of 2 drops of test-solution of sulphide of ammonium should not cause a black coloration (lead and iron). The remaining liquid should leave no fixed residue on evaporation and gentle ignition (non-volatile metals). When diluted with 5 volumes of water, it should not liberate iodine from test-solution of iodide of potassium (abs. of chlorine), nor should 10 C.c. of the diluted acid be precipitated within five minutes after the addition of 20 drops of test-solution of chloride of barium (sulphuric acid). If another portion of the diluted acid be treated with test-zinc, the evolved gas should not blacken paper wet with test-solution of nitrate of silver (sulphurous or arsenous acid).

The percentage strength can be ascertained by means of standard sodium hydrate solution.

Strength.—The various official hydrochloric acids compare as follows:

Pharmacopœia.	Per cent. HCl.	Specific gravity at 15° C. (water at +4°C. = 1.000.)	Number of parts representing 36.4 parts of HCl.
France (1884)-----	34.40	1.171	106.1
U. S. (1882)-----	31.90	1.160	114.4
Gt. Britain (1885)-----	31.90	1.160	114.4
Germany (1882)-----	25.00	1.124	146

Composition.—Absolute HCl contains 97.26 per cent. of chlorine and 2.74 per cent. of hydrogen.

One hundred parts of the official hydrochloric acid of the U. S. Pharmacopœia contains 81 parts of chlorine.

Uses.—For the preparation of certain other chlorides, chlorine, diluted hydrochloric acid, nitrohydrochloric acid, etc.

Action on metals.—Dissolves iron and zinc readily. Warm hydrochloric acid dissolves tin.

Saturating power.—100 parts of the official (U. S.) hydrochloric acid, containing 81.9 per cent. of HCl, will saturate alkalies as follows:

Potassa (100 per cent. KOH), 49.06 parts-----	} Yielding 65.20 parts of potassium chloride.
Potassa (90 per cent.), 54.51 parts-----	
Solution of potassa (5 per cent.), 981.2 parts	
Potassium carbonate (81 per cent.), 74.65 parts	
Potassium carbonate (100 per cent.), 80.47 parts	
Potassium bicarbonate (100 per cent.), 87.64 parts	} Yielding 51.18 parts of sodium chloride.
Soda (100 per cent. NaOH), 85.05 parts-----	
Soda (90 per cent.), 88.97 parts-----	
Solution of soda (5 per cent.), 701.16 parts---	
Sodium carbonate (100 per cent.), 125.40 parts	
Sodium carbonate (96 per cent.), 130.60 parts.	
Sodium bicarbonate (100 per cent.), 73.62 parts	
Sodium bicarbonate (99 per cent.), 74.86 parts	

Ammonia (NH ₃), 14.898 parts.....	} Yielding 46.80 parts of ammonium chloride.
Ammonia water (10 per cent.), 148.98 parts...	
Ammonia water, stronger (28 per cent.), 53.21 parts.....	
Ammonium carbonate, 45.86 parts.....	

Commercial muriatic acid.—This is impure hydrochloric acid, more or less yellow from iron and other impurities. It contains also sulphuric and sulphurous acids, and arsenic, as well as free chlorine. The several strengths sold by manufacturers in the United States are :

18° Beaumé=	1.14 sp. gr.=	28 per cent.
20° Beaumé=	1.16 sp. gr.=	32 per cent.
22° Beaumé=	1.18 sp. gr.=	35.5 per cent.

A carboy of this acid is about 120 lbs.

Specific Gravity and Percentage Strength of Solutions of HCl.

(Kolb.)

Per cent. HCl.	Sp. gr. 60°.	Sp. gr. 15°.
2.22	1.0116	1.0103
3.80	1.0202	1.0189
6.26	1.0335	1.0310
11.02	1.0581	1.0557
15.20	1.0802	1.0751
18.67	1.0988	1.0942
20.91	1.1101	1.1048
23.72	1.1258	1.1196
25.96	1.1370	1.1308
29.72	1.1569	1.1504
31.50	1.1666	1.1588
34.24	1.1806	1.1730
36.68	1.1931	1.1844
38.67	1.2026	1.1938
40.51	1.2110	1.2021
41.72	1.2165	1.2074
43.09	1.2216	1.2124

DILUTED HYDROCHLORIC ACID.

ACIDUM HYDROCHLORICUM DILUTUM.

Hydrochloric acid, by weight.....	6 parts.
Distilled water, by weight.....	13 parts.

Pour the acid into the water, and preserve the product in glass stoppered bottles.

Description.—Diluted hydrochloric acid contains 10 per cent. of absolute hydrochloric acid. It has the sp. gr. 1.049, and should respond to the same reactions and tests as hydrochloric acid. Its sp. vol. is 0.953.

Test.—To neutralize 10 C.c. of this acid 28.8 C.c. of normal sodium hydrate solution should be required.

Saturating power.—100 parts of the official (U. S.) diluted hydrochloric acid, containing 10 per cent. of HCl, will saturate alkalies as follows:

Potassa (90 per cent.), 17.09 parts.....	} Yielding 20.44 parts of potassium chloride.
Solution of potassa (5 per cent.), 807.69 parts.....	
Potassium carbonate (81 per cent.), 23.40 parts.....	
Potassium bicarbonate, 27.47 parts.....	
Soda (90 per cent.), 12.21 parts.....	} Yielding 16.05 parts of sodium chloride.
Solution of soda (5 per cent.), 219.78 parts.....	
Sodium carbonate (96 per cent.), 40.92 parts.....	
Sodium bicarbonate (99 per cent.), 28.31 parts.....	
Ammonia water (10 per cent.), 46.70 parts.....	} Yielding 14.87 parts of ammonium chloride.
Ammonia water, stronger (28 per cent.), 16.68 parts.....	
Ammonium carbonate, 14.88 parts.....	

NITROHYDROCHLORIC ACID.

ACIDUM NITROHYDROCHLORICUM.

[NITROMURIATIC ACID.]

Nitric acid, by weight.....	4 parts.
Hydrochloric acid by weight.....	15 parts.

Mix the acids in a large glass beaker, and, when effervescence has ceased, pour the mixture into a glass stoppered bottle, which should not be more than half filled. Keep it in a cool, dark place.

Reaction.— $\text{HNO}_3 + 3\text{HCl} = \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O}$.

Notes.—When strong nitric and hydrochloric acids are mixed both decompose, and free chlorine is formed in the liquid, which, therefore, is capable of dissolving gold, and has long been known under the name of "aqua regia." The medicinal value of the preparation also depends upon the free chlorine (and nitrosyl chloride) it contains. The Pharmacopoeial direction to keep it in bottles not more than half filled is intended to prevent the possible bursting of the bottle should the evolution of gas not have been completed before it was bottled. The effervescence which always takes place should be allowed to cease before the product is bottled, the acids should be cold when mixed, and the finished preparation should be kept in a cool place.

Care must be exercised in handling this acid. Chemical action must be completed before it, or any mixture containing it, should be dispensed.

Description.—A golden-yellow fuming and extremely corrosive liquid, having a strong odor of chlorine and a strongly acid reaction. Wholly volatilized by heat. Readily dissolves gold leaf. A drop of nitrohydrochloric acid added to test-solution of potassium iodide, liberates iodine in abundance.

DILUTED NITROHYDROCHLORIC ACID.

ACIDUM NITROHYDROCHLORICUM DILUTUM.

Nitric acid, by weight.....	4 parts.
Hydrochloric acid, by weight.....	15 parts.
Distilled water.....	76 parts.

Mix the undiluted acids in a large glass beaker, and, when effervescence has ceased, add the distilled water. Keep the product in a glass stoppered bottle in a cool place.

Notes.—The chemical reaction has been explained in the preceding article. It does not take place except when undiluted acids are used, and the reaction must be entirely completed before the water is added.

Description.—A colorless or faintly yellow liquid, odorless, or having a slight odor of chlorine, and a very acid taste and reaction. Wholly volatilized by heat. Liberates iodine from test-solution of potassium iodide.

POTASSIUM CHLORIDE.

POTASSII CHLORIDUM.

$KCl = 74.4.$

Exists in combination with magnesium chloride as *carnallite* in the great salt mines at Stassfurth, Germany.

Experimentally it may be made as follows:

Potassium bicarbonate.....	10 parts.
Water	20 parts.
Diluted hydrochloric acid, sufficient.	

Put the potassium bicarbonate in a porcelain capsule, add the water, and heat until effervescence ceases. Then gradually add hydrochloric acid until the liquid becomes neutral to litmus paper. This will require about 36.4 parts of the official diluted hydrochloric acid. Filter, and evaporate to dryness, stirring constantly toward the close, until a granular salt remains.

It is white, or colorless, inodorous, and has a pure saline taste. Soluble in 3 parts of cold and 2 parts of boiling water.

The crude potassium chloride from Stassfurth is very largely employed for the manufacture of other potassium salts.

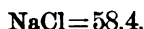
Tests.—The crystals should be completely and readily soluble in cold water, but not in absolute alcohol. The solution should be neutral. .186 Gm. should require 25 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

Test for traces of sodium by flame, and for traces of sulphates by solution of barium chloride.

Specific Gravity and Percentage Strength of Solutions of KCl.

(Gerlach.)

Per cent. of KCl.		Sp. gr. 15°.
5	-----	1.03250
10	-----	1.06580
15	-----	1.10036
20	-----	1.13608

SODIUM CHLORIDE.**SODII CHLORIDUM.**

Occurs native in extensive beds as *rock salt*, and also contained in saline springs and in sea-water. Large quantities are obtained in various parts of the United States.

Description.—Appears in commerce as a coarse white crystalline powder, in coarse grains for household use, and for the preservation of meats on the large scale, and in masses of rock salt. The last form is often impure and highly colored.

Tests.—The pure salt should be perfectly dry and easily soluble in water. 5 Gm. dissolved in water should leave a scarcely weighable sediment on filtration. Test a portion of the solution for sulphates by addition of a few drops of hydrochloric acid and solution of barium chloride. Test another portion of the solution for alkaline earth metals by addition of ammonia water to alkaline reaction, and solution of ammonium carbonate; a precipitate should not form.

.1168 Gm. of the dry salt should require 20 C.c of $\frac{N}{10}$ silver nitrate solution for precipitation.

Specific Gravity and Percentage Strength of Solutions of NaCl.
(Gerlach.)

Per cent. of NaCl.	Sp. gr. 15°.
1	1.0072
2	1.0145
3	1.0217
4	1.0290
5	1.03623
6	1.0437
7	1.0511
8	1.0585
9	1.0659
10	1.07335
15	1.1114
20	1.15107
25	1.19228

LITHIUM CHLORIDE.**LITHII CHLORIDUM.**

Prepared by neutralizing hydrochloric acid with lithium carbonate, filtering, and evaporating to dryness during constant stirring so as to

obtain a granulated salt; 37 parts of lithium carbonate require 364 parts of diluted hydrochloric acid.

Description.—Obtained as clear crystals or as white granules. Very deliquescent and very easily soluble in alcohol.

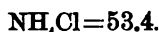
Tests.—Completely soluble in water and alcohol. It is precipitated from the aqueous solution, made alkaline by sodium hydrate, as fine crystals of phosphate by addition of solution of sodium phosphate.

.0848 Gm. of the dry salt should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

AMMONIUM CHLORIDE.

AMMONII CHLORIDUM.

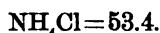
[MURIATE OF AMMONIA. SAL AMMONIAC.]



Prepared from gas liquor, the ammonia contained in that liquor being neutralized with hydrochloric acid. By sublimation the chloride is freed from most of the impurities derived from the crude materials. It usually occurs in solid crystalline masses, more or less discolored by iron.

PURIFIED AMMONIUM CHLORIDE.

AMMONII CHLORIDUM PURIFICATUM.



Crude ammonium chloride	20 parts.
Ammonia water	1 part.
Water	30 parts.

Dissolve the ammonium chloride in the water with the aid of heat, add the water of ammonia, continue the heat a few minutes, filter, and evaporate the filtrate to dryness with constant stirring.

The object of adding the ammonia is to precipitate any iron present.

Description.—A white crystalline powder, very easily soluble in water, but not hygroscopic.

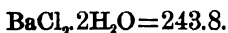
Tests.—Should be completely volatile without odor of organic substances.

The solution in water should give no test for sulphates when acidified with hydrochloric acid and treated with barium chloride.

.1068 Gm. should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

Specific Gravity and Percentage Strength of Solutions of NH_4Cl .

Per cent. of NH_4Cl .	(Gerlach.)	Sp. gr. 15°.
5	-----	1.0158
10	-----	1.0308
15	-----	1.0452
20	-----	1.0593
25	-----	1.0730

BARIUM CHLORIDE.**BARII CHLORIDUM.**

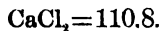
Prepared by neutralizing hydrochloric acid with barium carbonate. The filtered solution is acidified with HCl and evaporated to crystallization. The concentrated solution may also be precipitated by alcohol, which will hold the chlorides of calcium and strontium in solution.

Description.—Colorless crystals, which lose their water at 118°C .

They are readily soluble in water, but insoluble in strong alcohol.

Tests.—The solution in water should be clear, and should be completely precipitated by dilute sulphuric acid, or solution of potassium chromate.

.2438 Gm. should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

CALCIUM CHLORIDE.**CALCII CHLORIDUM.**

Prepared by neutralizing hydrochloric acid with calcium carbonate, filtering, evaporating to dryness, and fusing the residue at a low red heat.

Description.—So prepared it forms a hard white semi-transparent mass very soluble in water. Another form is obtained by heating the crystallized salt to 200°C . It contains two molecules of water, is porous, and is employed in drying gases and organic liquids. A third form has the constitution $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and consists of transparent crystals.

All forms are very quickly soluble in water.

Tests.—The water solution should be completely precipitated by solution of ammonium oxalate.

After precipitation of the calcium by ammonia water and ammonium carbonate the filtrate should give no test for magnesium on addition of solution of sodium phosphate.

20 C.c. of $\frac{N}{10}$ silver nitrate solution precipitates .1108 Gm. of the pure salt (anhyd.)

SOLUTION OF CALCIUM CHLORIDE.

LIQUOR CALCII CHLORIDI.

White marble, in powder..... 250 Gm.
 Hydrochloric acid..... 500 C.c.
 Water..... 400 C.c.

Mix the acid and water; add the marble dust, a little at a time; when effervescence has nearly ceased, heat the mixture over a water-bath until no more marble dissolves. Let settle. Decant the clear liquid and evaporate to dryness in a tared capsule; dissolve the residue in one and one-half times its weight of distilled water. Filter.

Reaction.— $\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$.

Specific Gravity and Percentage Strength of Solutions of CaCl_2 .

(Gerlach.)

Per cent. of CaCl_2 .	Sp. gr. 15°.
5	1.0426
10	1.0870
15	1.1386
20	1.1822
25	1.2337
30	1.2879
35	1.3448

ZINC CHLORIDE.

ZINCI CHLORIDUM.

$\text{ZnCl}_2 = 135.7$.

Prepared by dissolving zinc in hydrochloric acid, and evaporating the solution to dryness and fusion, and then allowing the product to cool. See remarks under solution of zinc chloride.

Description.—Hard, dirty white masses, which are very deliquescent, forming a clear solution with water.

Also soluble in alcohol. Very sharp, caustic taste, with acid reaction.

Tests.—The solution in water should give a perfectly white precipitate with ammonium sulphide, or solution of potassium ferrocyanide.

Should be precipitated white by solution of ammonium carbonate, and soluble in excess.

SOLUTION OF CHLORIDE OF ZINC.

LIQUOR ZINCI CHLORIDI.

An aqueous solution of chloride of zinc (ZnCl_2 , 135.7), containing about 50 per cent. of the salt.

Zinc, granulated.....	20 parts.
Nitric acid.....	1 part.
Precipitated carbonate of zinc.....	1 part.
Hydrochloric acid, distilled water, each sufficient.	

To the zinc, contained in a bottle, add gradually enough hydrochloric acid to dissolve it; filter the solution, add the nitric acid, evaporate to dryness, and bring the dry mass to fusion. Let it cool, dissolve it in 15 parts of distilled water, add the precipitated carbonate of zinc, and agitate the mixture occasionally during twenty-four hours. Finally, filter through washed asbestos free from iron, and pass enough distilled water through the filter to make the product weigh 80 parts.

Reaction.— $\text{Zn} + 2\text{HCl} = \text{ZnCl}_2 + \text{H}_2$.

Notes.—The metal dissolves with evolution of heat. Instead of adding the acid to the zinc, the metal may be gradually added to the acid. After the acid has been saturated the solution is digested with an excess of zinc to precipitate any foreign metals present (Cu, Pb, As, Cd). Iron and manganese, however, if present, are not precipitated by that means; they are removed by shaking the solution with zinc carbonate after first converting the ferrous into ferric chloride by means of nitric acid. The solution is evaporated to dryness and the salt fused to remove any excess of nitric acid. When the fused chloride is redissolved in water and the solution treated with zinc carbonate, the iron is separated as ferric hydrate.

Solution of zinc chloride cannot be filtered through paper, because the latter swells until its pores are closed and is then corroded. It may be filtered through powdered and washed glass, or through purified asbestos. Decantation is sometimes sufficient. A dilute solution may be filtered through paper, but the organic substances then taken up by it blacken the product as soon as sufficiently concentrated by evaporation.

Description.—A heavy, strongly caustic solution, which should mix with alcohol without precipitation. It has the sp. gr. 1.555, and the sp. vol. 0.643.

Tests.—As for the solid substance.

Specific Gravity and Percentage Strength of Solutions of ZnCl_2 .

(Kremers.)

Per cent. of ZnCl_2 .		Sp. gr. 19.5°.
18.876	-----	1.1275
25.819	-----	1.2466
37.483	-----	1.3869
49.257	-----	1.5551

SOLUTION OF ALUMINIUM CHLORIDE.**LIQUOR ALUMINII CHLORIDI.**

Calcium chloride.....	50 Gm.
Alum, in powder.....	100 Gm.
Water, sufficient.	

Dissolve the calcium chloride in 250 C.c. of water, and the alum in 750 C.c. of boiling water. Mix the solutions. Filter, rejecting the precipitated calcium sulphate. Add enough water to the filtrate to make it measure one liter.

Notes.—This solution is contaminated with potassium chloride and sulphate, but is sufficiently pure to be used for disinfecting purposes.

FERROUS CHLORIDE.**FERRI CHLORIDUM VIRIDE.**

Iron wire.....	15 Gm.
Hydrochloric acid.....	50 C.c.
Distilled water.....	30 C.c.

Dissolve the iron in the acid and water, previously mixed; when effervescence has ceased, heat to boiling. Let settle, decant, wash the undissolved iron with a little water, adding the washings to the decanted liquor, filter while hot, and crystallize. Remove the crystals from the mother liquor, drain them in a funnel, and put them at once in a bottle.

Reaction.— $\text{Fe}_2 + 4\text{HCl} = 2\text{FeCl}_2 + 2\text{H}_2$.

Notes.—Ferrous chloride is in green crystals, which soon become brown from oxidation.

One hundred Gm. of official hydrochloric acid yields about 87 Gm. of ferrous chloride; and 100 C.c. of the acid yields about 100 Gm.

GLYCERITE OF FERROUS CHLORIDE.**GLYCERITUM FERRI CHLORIDI VIRIDIS.**

Iron wire.....	15 Gm.
Hydrochloric acid.....	50 C.c.
Distilled water.....	30 C.c.
Glycerin.....	70 C.c.

Dissolve the iron in the acid and water, previously mixed; when effervescence has ceased, heat to boiling. Let settle, decant, wash the undissolved iron with a little water, adding the washings to the decanted liquor; filter; add the glycerin and evaporate the mixture until reduced to 100 C.c.

Each C.c. contains 0.50 Gm. of ferrous chloride.

FERRIC CHLORIDE

FERRI CHLORIDUM.



Iron wire, cut into small pieces..... 15 parts.
 Hydrochloric acid..... 86 parts.
 Nitric acid, distilled water, each sufficient.

Put the iron into a flask capable of holding two or three hundred parts of water. Add 54 parts of hydrochloric acid diluted with 25 parts of water. Set it aside in a warm place until effervescence ceases. Heat to the boiling point, filter, and, having rinsed the flask and undissolved iron with a little hot water, pass the rinsings also through the filter. Add 27 parts of hydrochloric acid to the filtrate, and add this mixture, a little at a time, to 8 parts of nitric acid contained in a capacious porcelain dish, waiting after each addition until effervescence subsides before adding more. After effervescence has ceased, heat the liquid over a sand-bath until it is free from nitrous odor and ceases to give a blue precipitate with test-solution of potassium ferricyanide. So long as this reagent causes a blue precipitate or a blue color, more nitric acid must be cautiously added and the heating continued, the excess of nitric acid to be driven off. When the liquid is free from ferrous salt, and free from nitrous odor, add 5 parts of hydrochloric acid and enough distilled water to make the whole weigh 80 parts. Set this aside in a porcelain dish, covered with a piece of glass, until it forms a solid, crystalline mass.

To loosen the mass from the dish, warm it gently. Having removed the chloride, break it into pieces, and keep it in a glass stoppered bottle, protected from light.

Reactions.—First, $\text{Fe}_2 + 4\text{HCl} = 2\text{FeCl}_2 + 2\text{H}_2$;
 then, $6\text{FeCl}_2 + 6\text{HCl} + 2\text{HNO}_3 = 3\text{Fe}_2\text{Cl}_6 + \text{N}_2\text{O}_2 + 4\text{H}_2\text{O}$.

Notes.—The iron is readily dissolved by the hydrochloric acid especially in the beginning; as the solution becomes charged with ferrous chloride, however, the action is slower and it is advantageous to promote it by the aid of heat. In

order that the density of the solution of ferrous chloride may not be so great as to retard the chemical action, the Pharmacopœia directs that the hydrochloric acid be diluted before the iron is added. The evolution of hydrogen may cease before all the HCl is decomposed by the iron at the ordinary temperature, but when the liquid is brought to the boiling point the acid is completely saturated. Some ferric chloride is formed before the acid is saturated, especially if the iron was rusty; but after boiling the liquid with the excess of iron present the solution contains ferrous salt only.

The solution of ferrous chloride is then to be treated with hydrochloric and nitric acids to convert it into ferric salt. When the solution is concentrated this may be accomplished at little above ordinary room temperature. When the solution is dilute, on the other hand, a temperature near the boiling point is required to complete the reaction. A good rule is to evaporate the solution of ferrous chloride until it has about 1.30 sp. gr., and after adding the additional quantity of hydrochloric acid prescribed, to add this solution slowly, a little at a time, to the nitric acid. If all of the solution of ferrous chloride is added at once, the reaction is too violent, the red fumes being evolved so copiously and suddenly that the liquid may boil over. The most suitable temperature at which the reaction may be carried out is between 100° and 110° C. (212° to 230° F.).

A small excess of nitric acid is unavoidable if the solution is to be entirely free from ferrous salt. This excess of nitric acid must be evaporated away, which is not an easy matter. A greenish brown coloration with test-solution of potassium ferricyanide is allowable, indicating merely traces of ferrous salt. But even then the excess of nitric acid liable to be present requires considerable evaporation to get rid of it. When the solution of ferric chloride is at last perfectly free from nitrous odor, and contains not more than traces of ferrous salt, the last addition of hydrochloric acid is made, and the distilled water added. This hydrochloric acid is added to prevent the formation of basic chloride.

The Pharmacopœia prescribes that the solution of ferric chloride be evaporated down to a given quantity by weight. It may preferably be evaporated down until a small sample taken out and cooled no longer gives off acid vapors in the air, or has a pronounced odor of HCl, and the liquid has about 1.62 to 1.65 sp. gr. at 25° C. (77° F.). This procedure is always necessary in cases where any portion of the liquid has been lost by accident at any stage of the process.

The chloride crystallizes readily, even within twelve hours, if of proper strength; but may not solidify for several weeks if too strong. When the evaporation has been carried too far, the liquid does not contain enough water of crystallization, and in that case it must be placed in a cool, moist atmosphere, from which the necessary additional moisture may be absorbed. A solution containing just enough hydrochloric acid crystallizes more readily than one that is not acid enough, and yields a lighter-colored and harder crystalline mass. The crystallization also proceeds more satisfactorily in a loosely covered dish than in a closely covered vessel.

Description.—A yellow crystalline mass, deliquescent, and readily soluble in water and alcohol. The solutions have an acid reaction.

Tests.—The solution should be completely precipitated by slight excess of ammonia water.

Solution of potassium ferricyanide should give only a brownish color, and not a blue.

To detect nitric acid, left by the process of preparation, add a few C.c. of strong sulphuric acid to an equal volume of solution. When the mixture has cooled, place in it a crystal of ferrous sulphate. The appearance of a brownish color or zone in the bottom of the test tube would be due to the reduction of nitric acid.

Composition.—Ferric chloride as obtained by the official process contains 12 molecules (about 40 per cent.) of water, and about 60 per cent. of anhydrous ferric chloride. It contains 20.7 per cent. of iron and 39.3 per cent. of chlorine.

AMMONIO-FERRIC CHLORIDE.**FERRI ET AMMONII CHLORIDUM.****[FLORES MARTIS.]**

Ferric chloride	20 Gm.
Ammonium chloride	180 Gm.
Diluted hydrochloric acid	10 C.c.
Distilled water	250 C.c.

Dissolve, filter, and evaporate the filtrate over a water-bath, during constant stirring, to dryness.

Put the dry product at once in a glass stoppered bottle and keep it protected from light.

An orange yellow, deliquescent powder.

SOLUTION OF FERRIC CHLORIDE.**LIQUOR FERRI CHLORIDI.**

An aqueous solution of ferric chloride, containing 37.8 per cent. of the anhydrous salt (Fe_2Cl_6), corresponding to 62.98 per cent. of crystalline ferric chloride ($\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$), and containing also some free hydrochloric acid.

Iron wire	15 parts.
Hydrochloric acid	86 parts.
Nitric acid, distilled water, each sufficient.	

Dilute 54 parts of the hydrochloric acid with 25 parts of distilled water; saturate it with iron, and oxidize the ferrous salt to ferric by means of 27 parts of hydrochloric acid and 8 parts of nitric acid, as described under Ferric Chloride. When the solution no longer contains ferrous salt, and all nitrous odor has been dissipated, add 5 parts of hydrochloric acid and enough distilled water to make the total product weigh 100 parts.

Notes.—The reactions, and the several steps of the process, are explained under the title, Ferric Chloride.

A solution of ferric chloride cannot be permanent without the presence of free hydrochloric acid. In the absence of a sufficient quantity of HCl , a basic ferric chloride is formed, which precipitates. To redissolve this yellow basic salt requires more hydrochloric acid than it takes to prevent its formation. Continued heating results in the loss of HCl and the formation of yellow oxychloride; if, however, sufficient HCl is present, no precipitate is formed, but the solution becomes darker in color, a ferric chloride with 5 molecules of water being formed. After standing some time, however, the darkened solution resumes its original color, and then contains the chloride with 12 molecules of water. Weak solutions are more readily altered, and when darkened by heating do not resume a lighter color on standing.

Sunlight decomposes ferric chloride slowly into ferrous chloride and chlorine. In the presence of organic substances, such as alcohol or ether, this reduction is more rapid.

Solution of chloride of iron may also be made by dissolving ferric oxide or ferric hydrate in hydrochloric acid. The oxidation of ferrous to ferric chloride may be effected by conducting chlorine gas into the solution of ferrous chloride, or by means of hydrochloric acid and potassium chlorate. The last mentioned method is attended with danger from explosion of the chloric acid.

In preparing ferric hydrate from the official solution of ferric chloride 100 parts of this solution require about 135 parts of ammonia water (an excess being necessary); 100 parts of solution of ferric chloride, containing 87.8 per cent. of Fe_2Cl_6 , will yield 24.93 parts of ferric hydrate ($\text{Fe}_2(\text{OH})_6$). Official solution of ferric chloride contains slightly more than 18 per cent. of metallic iron, corresponding to 18.63 per cent. of ferric oxide, and 100 parts of the solution equals 162 parts of solution of ferric sulphate in contents of metallic iron.

Strength.—The relative strengths of the various official solutions of ferric chloride are as follows:

Pharmacopœia.	Sp. gr.	Per cent. Fe_2Cl_6 .
U. S.	1.405	87.8
Br.; strong.	1.420	41
Br.; ordinary.	1.110	18
German.	1.281	29
French.	1.260	26
Swedish.	1.300	30

Description.—A clear reddish brown solution, with acid reaction. Sp. gr. 1.405; sp. vol. 0.712.

Tests.—As given for the crystals.

Specific Gravity and Percentage Strength of Solutions of Fe_2Cl_6 .

Per cent. of Fe_2Cl_6 .	(Franz.)	Sp. gr. 17°5.
5	-----	1.0365
10	-----	1.0734
15	-----	1.1134
20	-----	1.1542
25	-----	1.2052
30	-----	1.2568
35	-----	1.3093
40	-----	1.3622
45	-----	1.4242
50	-----	1.4867
55	-----	1.5582
60	-----	1.6317

BRITISH STRONG SOLUTION OF FERRIC CHLORIDE.

LIQUOR FERRI PERCHLORIDI FORTIOR; B.

Iron wire 80 Gm.
 Hydrochloric acid 410 C.c.
 Nitric acid 30 C.c.
 Distilled water, sufficient.

Put the iron in a flask; add a mixture of 250 C.c. of hydrochloric acid and 140 C.c. of water; digest at a moderate heat until effervescence ceases; then heat to boiling; filter the liquid from the undissolved iron, rinsing the flask and contents with a little water and pouring this over the filter; mix the filtrate with 140 C.c. of hydrochloric acid; add the mixture very slowly to the nitric acid contained in a capacious porcelain dish, promoting the evolution of the red fumes, if necessary, by a slight application of heat. Evaporate the product until no more nitrous vapors escape and a precipitate begins to form; then add 20 C.c. of hydrochloric acid and sufficient distilled water to make the final product measure 350 C.c.

Description.—Sp. gr. 1.42; sp. vol. 0.704. Each 10 C.c. of the solution contains 2 Gm. of iron.

TINCTURE OF FERRIC CHLORIDE.

TINCTURA FERRI CHLORIDI.

Solution of chloride of iron.....	35 parts.
Alcohol.....	65 parts.

Mix the liquids and let the mixture stand in a closely covered vessel for at least three months; then transfer it to glass stoppered bottles.

Notes.—It is to be observed that the alcohol is undiluted; the solution of chloride of iron contains free hydrochloric acid, and this acting upon the alcohol gives rise to the formation of chlorinated ether compounds, which are considered by some to be valuable constituents of the preparation. These compounds are formed very slowly, and hence the direction of the Pharmacopœia to allow the mixture to stand at least three months.

Tincture of chloride of iron when recently prepared is considerably darker than it will be after standing for some weeks or months exposed to light. This is due to a reduction of the ferric to ferrous chloride, and owing to the presence of alcohol in the preparation, the formation of ferrous chloride is inevitable. Hence the official test requiring the absence of ferrous salt is one that the preparation never can satisfy.

ETHEREAL TINCTURE OF CHLORIDE OF IRON.

TINCTURA FERRI CHLORIDI ÆTHERICA.

Ferric chloride.....	20 Gm.
Distilled water.....	20 C.c.
Ether.....	160 C.c.
Alcohol.....	500 C.c.

Dissolve the chloride in the water in a bottle; add the ether; cork the bottle, shake well, and set the mixture aside for twenty-four hours. Separate the clear ethereal liquid; mix it with the alcohol in a glass stoppered bottle, and set the mixture in the sunlight, shaking it occasionally. When the yellow color has entirely disappeared, put the

mixture in a shaded place, removing the stopper frequently, until the yellow color returns.

Notes.—The preparation contains ferrous chloride, basic ferric chloride, ethyl chloride, aldehyde, and hydrochloric acid. It is official in the German Pharmacopœia.

Should be kept in well closed bottles in a dark place.

TINCTURE OF CITRO-CHLORIDE OF IRON.

"TINCTURA FERRI CITRO-CHLORIDI"

(New York and Brooklyn Formulary.)

Solution of chloride of iron	25 C.c.
Citric acid	26 Gm.
Sodium bicarbonate	28 Gm.
Alcohol	25 C.c.
Water, enough to make	100 C.c.

Dissolve the citric acid in 25 C.c. of water, heat to boiling, and gradually add the sodium bicarbonate. When effervescence has ceased, add the solution of chloride of iron. Let cool. Now add enough water to make the liquid measure 75 C.c.; finally add the alcohol.

Notes.—The greenish color, and the absence of styptic taste in this preparation, show that some chemical combination between the ferric chloride and the sodium citrate takes place.

SUBLIMED MERCUROUS CHLORIDE.

HYDRARGYRI CHLORIDUM MITE.

[CALOMEL.]

$\text{Hg}_2\text{Cl}_2 = 470.4.$

Mercuric sulphate	10 parts.
Mercury	7 parts.
Sodium chloride, dried	5 parts.
Boiling distilled water, sufficient.	

Moisten the mercuric sulphate with some of the water; add the mercury; triturate until metallic globules are no longer visible; add the sodium chloride and mix the whole thoroughly by long continued trituration. Sublime by a suitable apparatus. Wash the sublimate with boiling distilled water until the washings cease to be darkened by a drop of ammonium sulphhydrate. Dry it at not over 100°C. (212°F.).

Reaction.— $\text{HgSO}_4 + \text{Hg} = \text{Hg}_2\text{SO}_4$; then, $\text{Hg}_2\text{SO}_4 + 2\text{NaCl} = \text{Hg}_2\text{Cl}_2 + \text{Na}_2\text{SO}_4.$

Notes.—Sublimed calomel is yellowish white when prepared in small quantities and with the ordinary apparatus, as flasks or retorts. When prepared in large quantities, the condensation being effected in large chambers into which steam is injected, the product is nearly white, and more finely divided.

Calomel may also be made by triturating 4 parts of mercuric chloride with 3 parts of mercury until metallic globules are no longer to be seen, keeping the mixture moist with a little alcohol to prevent the poisonous powder from rising in the air; then drying the mixture at a moderate heat, and putting it into small bottles (about 200 C.c. capacity) with thin bottoms, the bottles to be only one-third filled, closing the necks of the bottles loosely with chalk stoppers, and subliming on a sand-bath, the heat to be at first moderate and gradually increased until the process is completed. The sublimate is crystalline and must be triturated with warm water a long time until reduced to an extremely fine powder, and free from mercuric chloride. This is levigated calomel.

If the mixture of mercuric chloride and mercury is carefully dried and heated over a sand-bath with constant stirring, this operation being performed under a hood, with a good draft, the moisture, mercuric chloride and mercury will pass off first, leaving nearly pure mercurous chloride, which is then sublimed as already described.

The heat must not be too high, for then the calomel is decomposed into mercury and mercuric chloride. As the sublimate is deposited immediately above the level of the sand, the bottles should be buried in the sand up to just above the level of their contents.

The bottle must be broken to remove the sublimate. When still warm it is best detached by moistening with a little water. After a few days it readily comes off without moistening.

Description.—A fine white powder with *very slight* tinge of yellow. It is without taste, and is insoluble in water and alcohol. It volatilizes completely by heat. Sp. gr. 6.56.

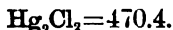
Tests.—Blackened by addition of ammonia water.

Shake several Gm. with water, filter, acidify the filtrate with a drop of hydrochloric acid, and immerse in it a strip of copper. This should not become coated with a gray film. A second water solution, prepared in the same way, should not blacken on addition of hydrogen sulphide.

PRECIPITATED MERCUROUS CHLORIDE.

HYDRARGYRI CHLORIDUM MITE PRÆCIPITATUM.

[PRECIPITATED CALOMEL.]



Mercury..... 300 Gm.
Nitric acid..... 270 C.c.
Distilled water, hydrochloric acid, each sufficient.

Put the mercury in a tared flask; add 180 C.c. of nitric acid and 270 C.c. of water. Heat the flask moderately on a sand-bath, covering the mouth of the flask with a watch-glass, and continue the heat without interruption for one hour after red fumes have ceased to be evolved, or until the liquid begins to acquire a yellowish color and to become slightly turbid. Pour the solution of mercurous nitrate off from undissolved mercury.

Mix 90 C.c. of nitric acid with 1,800 C.c. of boiling distilled water, and add this mixture to the solution of mercurous nitrate while still hot.

Then let it cool. To 5 C.c. of the cold, diluted liquid, add gradually 5 C.c. of distilled water. If this addition of water should render the mercury solution turbid, more nitric acid should be gradually added to it until it will bear dilution with an equal volume of water without turbidity.

Ascertain the quantity of mercury contained in the liquid by washing, drying and weighing the undissolved portion remaining in the flask.

Take a quantity of hydrochloric acid equal to twice the weight of dissolved mercury; dilute it with 1,800 C.c. of water. To this acid liquid add gradually and with constant stirring the dilute solution of mercurous nitrate.

Wash the precipitate with cold distilled water, by affusion and decantation, until the washings no longer give an acid reaction to test-paper. Dry the product at a temperature not exceeding 40° C. (104° F.).

Reaction.— $3\text{Hg}_2 + 8\text{HNO}_3 = 3\text{Hg}_2(\text{NO}_3)_2 + \text{N}_2\text{O}_2 + 4\text{H}_2\text{O}$; and subsequently, $\text{Hg}_2(\text{NO}_3)_2 + 2\text{HCl} = \text{Hg}_2\text{Cl}_2 + 2\text{HNO}_3$.

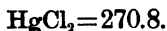
Notes.—The directions here given for testing the mercury solution to ascertain whether or not it can be further diluted without precipitation, and to add enough nitric acid to render dilution possible, are rendered necessary by the fact that otherwise the product might be contaminated by basic mercurous nitrate precipitated by the water mixed with the hydrochloric acid. Dilute liquids are necessary to prevent the formation of mercuric salt in the presence of the free nitric acid.

Precipitated calomel is bulkier than sublimated calomel, is a very finely divided powder, and, if well washed and carefully dried, entirely inodorous, tasteless, white, and free from mercuric chloride.

MERCURIC CHLORIDE.

HYDRARGYRI CHLORIDUM CORROSIVUM.

[CORROSIVE SUBLIMATE.]



Mercuric sulphate	20 parts.
Sodium chloride, dried	16 parts.
Black oxide of manganese, in fine powder....	1 part.

Reduce the mercuric sulphate and the sodium chloride, each, to fine powder, and, having mixed them and the oxide of manganese thoroughly by trituration in a mortar, put the mixture in an apparatus adapted for sublimation, and apply sufficient heat to cause vapors of mercuric chloride to rise into the less heated part of the apparatus which has been arranged for their condensation.

Reaction.— $\text{HgSO}_4 + 2\text{NaCl} = \text{HgCl}_2 + \text{Na}_2\text{SO}_4$.

Notes.—The black oxide of manganese is added to oxidize any mercurous salt which may be present in the mercury sulphate. Toward the close of the sublimation the heat is raised to near the fusing point of the sublimate in order to obtain a crystalline product.

Mercuric chloride can be obtained in fine crystals by slowly evaporating its solution in dilute alcohol.

When mercuric chloride is powdered it should be kept moist with alcohol to prevent the poisonous dust from rising.

Description.—A heavy crystalline salt, soluble in water and in alcohol. At a high heat it volatilizes unchanged.

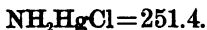
Tests.—When dissolved in water it should leave no residue.

The aqueous solution, acidified with hydrochloric acid, should give no precipitate with barium chloride, but should be precipitated completely by hydrogen sulphide. The aqueous solution gives a red precipitate with solution of potassium iodide, which should be completely soluble in excess.

AMMONIATED MERCURY.

HYDRARGYRUM AMMONIATUM.

[MERCUR-AMMONIUM CHLORIDE; WHITE PRECIPITATE.]



Mercuric chloride 50 Gm.

Ammonia water, distilled water, each sufficient.

Dissolve the chloride in 1,000 C.c. of warm distilled water; filter and allow to cool. Pour the filtrate gradually and during constant stirring into 75 C.c. of ammonia water, taking care that the ammonia shall remain in excess when all of the mercuric chloride has been added. Collect the precipitate at once on a filter, drain as much as possible, and then wash it twice, each time with a mixture of 40 C.c. of distilled water and 2 C.c. of ammonia water. Finally, dry the precipitate between filter paper in a dark place at a temperature not exceeding 30° C. (86° F.).

Reaction.— $\text{HgCl}_2 + 2\text{NH}_4\text{OH} = \text{NH}_4\text{Cl} + \text{NH}_2\text{HgCl} + 2\text{H}_2\text{O}$.

Notes.—When a solution of mercuric chloride is poured into ammonia water, the latter being in excess throughout, the official ammoniated mercury is formed.

When, however, the order of mixing the liquids is reversed, the ammonia water being added to the mercuric chloride, or when the mercuric chloride is present in excess over the proportion of ammonia used, the product will be, or will contain, $\text{NH}_2(\text{HgCl})_2\text{Cl}$ instead of NH_2HgCl . The $\text{NH}_2(\text{HgCl})_2\text{Cl}$ is, however, converted into the official mercurammonium chloride when allowed to remain in contact with an excess of ammonia for some time.

Mercurammonium chloride is perfectly white. A grayish color indicates that the solution of mercuric chloride was not filtered before adding it to the ammonia, whereby the calomel, which is always present in corrosive sublimate, gives rise to mercurous oxide. If warm liquids are used, or if the precipitate be washed with warm water or too long, or if ammonia is not present in the washing

and drying, the product will be more or less yellow from hydroxyl-dimercurammonium chloride ($\text{ClHg}_2\text{OH}_2\text{N}$). The same result follows if a too high temperature is used in drying. Exposure to light renders it grayish.

The preparation must be kept in well closed bottles, in a cool place, and protected from light.

Description.—Usually a fine white powder, insoluble in water and alcohol. The compound decomposes by application of heat.

Tests.—Heated with solution of potassium hydrate, ammonia is evolved and yellow mercuric oxide precipitated.

It should be completely soluble in solution of sodium thiosulphate, with evolution of ammonia. On heating, a red precipitate is thrown down, which becomes black on boiling (mercuric sulphide).

CHLORIDE OF GOLD AND SODIUM.

AURI ET SODII CHLORIDUM.

A mixture composed of equal parts of dry chloride of gold (AuCl_3) and sodium chloride.

Description.—An orange yellow powder, soluble in water. It is decomposed by heat, metallic gold being separated.

Tests.—Should contain 32.4 per cent. of pure gold. This can be determined by precipitating its solution with solution of ferrous sulphate, collecting, washing, drying and weighing the precipitate.

BISMUTH OXYCHLORIDE.

BISMUTHI OXYCHLORIDUM.

$$\text{BiOCl} = 258.9$$

Bismuth	140 Gm.
Nitric acid.....	230 C.c.
Sodium chloride	390 Gm.
Distilled water, sufficient.	

Mix the acid with 300 C.c. of water; dissolve the metal in the mixture. Dissolve the chloride of sodium in 4,000 C.c. of distilled water, and filter. Pour the acid solution of nitrate of bismuth gradually and with constant stirring into the solution of sodium chloride.

Wash the precipitate with distilled water, first by decantation and afterwards on a filter, until the washings are tasteless. Drain, and then dry the product between bibulous paper with the aid of gentle heat.

Reaction.— $\text{BiONO}_3 + \text{NaCl} = \text{NaNO}_3 + \text{BiOCl}$.

SOLUTION OF ANTIMONY CHLORIDE.**LIQUOR ANTIMONII CHLORIDI; B.**

Purified antimonious sulphide..... 100 Gm.
 Hydrochloric acid..... 500 C.c.

Dissolve the sulphide in the acid by putting them together in a porcelain capsule, stirring constantly, applying at first gentle heat, increasing the temperature as the evolution of gas slackens, and finally bring the liquid to the boiling point. Boil for fifteen minutes. Then remove the capsule from the source of heat, and filter the liquid through muslin, returning the portion which passes first until the filtrate becomes perfectly clear.

Evaporate the filtrate to 250 C.c., and put it in a glass stoppered bottle.

Sp. gr. 1.47; sp. vol. 0.680. It is a solution of SbCl_3 (molecular weight, 226.2) in hydrochloric acid.

Reaction.— $\text{Sb}_2\text{S}_3 + 6\text{HCl} = 2\text{SbCl}_3 + 3\text{H}_2\text{S}$.

Note.—The operation must be conducted under such conditions that the gas (H_2S) will be carried off through a flue, or it may be done out in the open air. Sometimes nitric acid is used with the hydrochloric acid.

OXYCHLORIDE OF ANTIMONY.**ANTIMONII OXYCHLORIDUM.**

When a solution of chloride of antimony is poured into water, the above named compound (formerly called *Algaroth's powder*) is precipitated.

The reaction and other details have been given under Antimony Oxide.

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CHAPTER XII.

BROMIDES.

The bromides of potassium, sodium, lithium, ammonium, calcium, zinc and iron are used in medicine and pharmacy. All of these are water soluble. Bromide of iron is made by the action of bromine on the metal in the presence of water; the other bromides are usually made by double decomposition.

HYDROBROMIC ACID.

ACIDUM HYDROBROMICUM.

$\text{HBr} = 80.8.$

Sulphuric acid.....	14 parts.
Potassium bromide.....	12 parts.
Distilled water, sufficient.	

Put two parts of the water in a porcelain dish capable of holding about 32 parts; stir the water into a rapid rotary motion; then add the sulphuric acid slowly and in a thin stream, continuing the stirring with a glass rod; when cool put the mixture into a bottle. Put the potassium bromide, previously reduced to coarse powder, in the dish; add 13 parts of water, heat the mixture by a sand-bath until the salt is dissolved, and while the solution is still hot add to it the sulphuric acid mixture, stirring briskly. Set aside for twenty-four hours. Decant the acid supernatant liquid (hydrobromic acid) from the crystals of potassium sulphate, and pour it into a suitable distilling flask. Wash the crystals with a little cold water, and add these washings to the acid.

Provide the flask with a perforated stopper and safety tube, and connect it with a well cooled receiver. Distil nearly to dryness. Dilute the distillate with distilled water to the required strength.

Reaction.— $2\text{KBr} + \text{H}_2\text{SO}_4 = 2\text{HBr} + \text{K}_2\text{SO}_4$.

By-product. The potassium sulphate may be washed with cold water, dried, and saved.

Properties.—The Pharmacopoeial "diluted hydrobromic acid" contains 10 per cent. of hydrogen bromide. It should be preserved in glass stoppered bottles. A stronger hydrobromic acid, containing 34 per cent. of HBr, is also in use, but is not official. Its specific gravity is 1.289.

The Pharmacopoeial acid has the specific gravity 1.070 at 15° C. (59° F.) compared with water at -4° C. (39° 2 F.) as 1,000 (Squibb). The Pharmacopoeial statement of the specific gravity, 1.077, is probably erroneous. Its specific volume is 0.934. The official descriptions and tests are as follows:

"A clear, colorless liquid, odorless, having a strongly acid taste and an acid reaction. Sp. gr. 1.077. By heat it is completely volatilized. On adding chlorine or nitric acid to diluted hydrobromic acid, bromine is liberated, which is soluble in chloroform or in disulphide of carbon, imparting to these liquids a yellow color. Test solution of nitrate of silver causes a white precipitate, insoluble in nitric acid and in water of ammonia, and sparingly soluble in stronger water of ammonia.

"On being kept for some time, the acid should not become colored; test-solution of chloride of barium should not produce a turbidity or precipitate (sulphuric acid)."

To neutralize 16.2 Gm. of diluted hydrobromic acid should require 20 C.c. of normal sodium hydrate solution.

Composition.—The absolute hydrobromic acid contains 98.75 per cent. of bromine and 1.25 per cent. of hydrogen.

Specific Gravity and Percentage Strength of Solutions of HBr.

(Biel.)

Per cent. of HBr.	Sp. gr. 15°.
1	1.008
2	1.015
3	1.023
4	1.030
5	1.038
6	1.046
7	1.053
8	1.061
9	1.069
10	1.077
11	1.085
12	1.093
13	1.102
14	1.110
15	1.119
16	1.127
17	1.136
18	1.145
19	1.154
20	1.163

Per cent. of HBr.	Sp. gr. 15°.
25	1.209
30	1.260
35	1.314
40	1.375
45	1.444
50	1.513

The hydrobromic acid of 34 per cent. strength can be conveniently diluted to 10 per cent. strength by mixing 5 parts of the strong acid with 12 parts of distilled water.

Saturating power.—100 parts of the official (U. S.) hydrobromic acid, containing 10 per cent. of HBr, will saturate:

Potassium bicarbonate, 12.37 parts	}	Yielding 14.70 parts of potassium bromide.
Potassium carbonate (81 per cent.), 10.54 parts.		
Sodium bicarbonate (99 per cent.), 10.50 parts.	}	Yielding 12.72 parts of sodium bromide.
Sodium carbonate (96 per cent.), 18.44 parts		
Ammonia water (10 per cent.), 21.04 parts	}	Yielding 12.10 parts of ammonium bromide.
Ammonia water, stronger (28 per cent.), 7.51 parts		
Ammonium carbonate, 6.49 parts		

POTASSIUM BROMIDE.

POTASSII BROMIDUM.

KBr=118.8.

Iron wire, cut	80 Gm.
Bromine	240 Gm.
Potassium bicarbonate	300 Gm.
Distilled water, sufficient.	

Digest the iron and 180 Gm. of bromine with 500 C.c. of water in a flask until all odor of bromine ceases and a green solution of ferrous bromide is obtained. Filter; add the remainder of the bromine to the filtrate, and dissolve.

Put the potassium bicarbonate into a dish with 1,000 C.c. of distilled water, heat until effervescence ceases, and then raise the heat to boiling. Add slowly to this boiling hot solution the filtered solution of the bromides of iron. Boil the mixture for fifteen minutes. Filter, and evaporate the filtrate to dryness, stirring constantly.

Reaction.— $3\text{Fe} + 6\text{Br} = 3\text{FeBr}_2$; then, $3\text{FeBr}_2 + 2\text{Br} = \text{FeBr}_2 \cdot \text{Fe}_2\text{Br}_4$; then, $\text{FeBr}_2 \cdot \text{Fe}_2\text{Br}_4 + 4\text{K}_2\text{CO}_3 = 8\text{KBr} + \text{FeO} \cdot \text{Fe}_2\text{O}_3 + 4\text{CO}_2$.

Notes.—The solution, after adding the iron bromide to the potassium carbonate, should be alkaline.

Ferrico-ferrous bromide is used instead of ferrous bromide, because the iron is then more easily and perfectly separated.

See also notes under Potassium Iodide.

Potassium bromide is also prepared by the following process:

Solution of potassa.....	2850 C.c.
Bromine, about	200 Gm.
Wood charcoal, in fine powder.....	100 Gm.
Boiling distilled water.....	1500 C.c.

Put the solution of potassa in a flask; add the bromine gradually, with constant agitation, until the liquid has acquired a permanently brown color. Evaporate to dryness; powder the residue and mix it well with the charcoal. Throw the mixture into a red hot iron crucible, and when reduced to a state of fusion, pour out the contents, let cool, dissolve it in the boiling water, filter, and set aside to crystallize. Drain the crystals and dry them in a warm place. Recover the salt contained in the mother liquor by evaporation to dryness, stirring constantly.

Reaction.— $\text{Br}_2 + 6\text{KOH} = 5\text{KBr} + \text{KBrO}_3 + 3\text{H}_2\text{O}$;
and then, $2\text{KBrO}_3 + 3\text{C}_2 = 2\text{KBr} + 6\text{CO}$.

See remarks under Potassium Iodide.

Description.—Colorless, cubical crystals having a sharp saline test. Very soluble in water. Slowly in alcohol.

Solutions of the pure salt have a neutral reaction.

Tests.—Complete solubility in water, and neutral reaction of the solution.

Test for bromates by pouring a little dilute sulphuric acid over the powdered salt; it should not turn yellow.

Test for iodides by dissolving about a Gm. in water and adding some starch paste. Then add carefully, so as not to mix the liquids, a few drops of chlorine water.

A blue color should not appear at the zone between the two liquids.

.2876 Gm. should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation. If more than this is required the presence of a chloride is indicated.

SODIUM BROMIDE.

SODII BROMIDUM.

$\text{NaBr} = 102.8$.

Iron wire, cut.....	80 Gm.
Bromine	240 Gm.
Sodium carbonate.....	450 Gm.
Distilled water, sufficient.	

Digest the iron and 180 Gm. of bromine with 500 C.c. of water in a flask until all odor of bromine has ceased, and the liquid becomes green. Filter, add the remainder of the bromine to the filtrate, and let it dissolve.

Dissolve the sodium carbonate in 1,000 C.c. of boiling distilled water, and add the solution of bromide of iron. Boil for fifteen minutes, filter, and evaporate the filtrate to dryness during constant stirring.

Notes.—The reactions are analogous to those occurring in the preparation of potassium bromide from bromide of iron and potassium carbonate.

The sodium bromide may also be made from bromine and solution of soda, as potassium bromide is prepared from bromine and solution of potassa.

Description.—Where the salt is deposited from hot concentrated solutions the crystals are anhydrous and cubical, while hydrated monoclinic crystals are deposited by slow evaporation of cold solutions. Both forms are readily soluble in water and alcohol.

Tests.—The reaction should be neutral (absence of carbonate). The solution in water should not become turbid on addition of a drop of hydrochloric acid and solution of barium chloride.

The tests for bromates and iodine are made as under Potassium Bromide.

.2056 Gm. should require 20 C.c. of $\frac{N}{10}$ solution of silver nitrate for precipitation.

LITHIUM BROMIDE.

LITHII BROMIDUM.



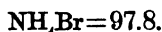
Prepared by three different methods:

(1) By neutralizing hydrobromic acid with lithium carbonate. (2) By double decomposition between lithium sulphate and potassium bromide, the potassium sulphate being separated by the addition of alcohol in which lithium bromide is soluble. (3) By treating a solution of ferrous bromide with lithium carbonate.

Description.—White salt, very soluble in water and alcohol.

AMMONIUM BROMIDE.

AMMONII BROMIDUM.



Iron wire	80 Gm.
Bromine	240 Gm.
Ammonia water	550 C.c.

Put the iron wire into a flask, add 1,000 C.c. of luke-warm water, and then gradually add 180 Gm. of the bromine. Put a loose plug of cotton into the neck of the flask, and gently agitate until a greenish

liquid is obtained, having no odor of bromine. Filter the solution of ferrous bromide, add to it the remainder of the bromine, and set aside until a perfect solution is formed. Pour this into the ammonia water previously diluted with 1,000 C.c. of distilled water. Shake well, heat the mixture on a water-bath for half an hour, and then filter. When the liquid has passed, wash the residue on the filter with a little boiling distilled water, adding the washings to the filtrate. Evaporate the filtrate in a porcelain dish until a pellicle begins to form. Then stir the contents with a glass rod, constantly, and continue the evaporation until a granular salt remains.



Notes.—Ammonium bromide may also be made by putting the bromine with four times its weight of water into a flask, and then adding the ammonia water cautiously, about one-thirtieth part at a time, until all has been added, and covering the mouth of the flask with a watch-glass when vapors are formed. When the liquid is free from bromine odor it is filtered, and evaporated to granulation, the reaction being: $3\text{Br}_2 + 8\text{NH}_3 = 6\text{NH}_4\text{Br} + \text{N}_2$.

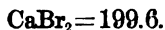
Description.—A white granular salt, which becomes yellowish by long exposure to the air and light. Readily soluble in water; slightly soluble in cold alcohol. The aqueous solution when treated with chlorine water should yield pure bromine, which dissolves in carbon bisulphide with pure yellow color, free from violet.

Tests.—Should volatilize completely without decomposition, when heated on platinum foil. Bromates and iodine should be tested for as under Potassium Bromide.

.1956 Gm. should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

CALCIUM BROMIDE.

CALCII BROMIDUM.



Ammonium bromide. 3 parts.
Lime. 1 part.

Slake the lime with 6 parts of water and triturate it in a mortar, adding enough water to form a liquid mixture. Dissolve the ammonium bromide in 8 parts of water, heat to the boiling point, and then add the milk of lime until the evolution of ammonia ceases. Then filter the solution and evaporate the filtrate to dryness, stirring constantly so as to produce a granulated salt.

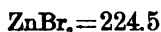


Description.—Prepared as above it is a white granular salt, deliquescent and very soluble in water and alcohol. It can be fused at a low red heat without decomposition.

Tests.—Should produce a perfectly clear solution with water. This solution should be neutral to test-paper. Test for bromates and iodine as under Potassium Bromide. .1996 Gm. of the dry salt should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

ZINC BROMIDE.

ZINCI BROMIDUM.



Zinc sulphate 8 parts.
 Potassium bromide 7 parts.
 Boiling distilled water, sufficient.

Dissolve the sulphate in 10 parts and the bromide in 6 parts of the water. Mix the solutions while hot. When cool add 40 parts of alcohol, and filter the mixture through asbestos. Evaporate the filtrate to dryness, and granulate the product.

Reaction.— $\text{ZnSO}_4 + 2\text{KBr} = \text{K}_2\text{SO}_4 + \text{ZnBr}_2$.

Description.—White granular powder, readily soluble in water and alcohol. Fuses without decomposition at a red heat.

Tests.—Should yield a clear solution when dissolved in water. This solution acidified with hydrochloric acid, should give no precipitate when treated with solution of barium chloride or with hydrogen sulphide.

Test for bromates and iodine in the usual way.

.2245 Gm. of the dry salt should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

SYRUP OF BROMIDE OF IRON.

SYRUPUS FERRI BROMIDI.

A syrupy liquid containing 10 per cent. of ferrous bromide (FeBr_2 , 215.6).

Iron, in the form of wire, cut into small pieces. 30 Gm.
 Bromine 75 Gm.
 Sugar, in coarse powder 600 Gm.
 Distilled water, sufficient.

Introduce the iron into a flask, add 200 C.c. of distilled water, and afterward the bromine. Shake the mixture occasionally, until the reaction ceases and the solution has acquired a green color and has lost the odor of bromine. Place the sugar in a porcelain dish and filter the solution of bromide of iron into the sugar. Rinse the flask and iron

wire with 90 C.c. of distilled water, and pass the washings through the filter into the sugar. Stir the mixture with a glass rod, heat it to the boiling point on a sand-bath, and, having filtered the syrup through paper into a tared bottle, add enough distilled water to make the product weigh 1,000 Gm. Lastly, shake the bottle, which should be completely filled, securely corked, and kept in a place accessible to daylight.

Notes.—The bromine must be added cautiously, as the reaction is sometimes violent. When too violent, the chemical action can be controlled by keeping the flask in cold water.

The preparation should be kept in small, glass stoppered bottles.

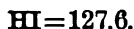
CHAPTER XIII.

IODIDES.

Prepared from iodine, potassium iodide, or iodide of iron. All are water soluble except the iodide of silver and mercurous iodide; mercuric iodide is, however, nearly insoluble, and iodide of lead requires nearly 200 parts of boiling water for its solution.

HYDRIODIC ACID.

ACIDUM HYDRIODICUM.



Hydrogen iodide may be prepared by decomposing potassium iodide with sulphuric or tartaric acid and distilling; or it may be made by treating iodine with hydrogen sulphide as directed in the formula for syrup of hydriodic acid.

Hydriodic acid decomposes readily, and becomes reddish brown from free iodine. It seems impossible to wholly prevent this decomposition.

Composition.—Contains over 99 per cent. of combined iodine.

SYRUP OF HYDRIODIC ACID.

SYRUPUS ACIDI HYDRIODICI.

A syrupy liquid, containing 10 per cent. of absolute hydriodic acid (HI, 127.6).

Iodine.....	10 Gm.
Alcohol.....	100 C.c.
Syrup.....	120 C.c.
Sugar.....	500 Gm.
Spirit of orange.....	6 C.c.
Distilled water.	

Dissolve the iodine in the alcohol, with a very gentle heat, in a loosely stoppered flask, avoiding loss of iodine from vaporization. Add the solution to the syrup previously mixed with 150 C.c. of distilled water, and pass through the mixture a current of hydrogen sulphide gas, until it acquires a pure yellowish color, and ceases to turn brown on shaking. Filter the liquid through white filter paper, returning the first portions until it runs off clear; wash the filter with a little distilled water, and evaporate the filtrate and washings in a tared porcelain dish, on a water-bath, at a temperature not exceeding 55°C . (181°F .), constantly stirring until all odor of the hydrogen sulphide has disappeared. Then set the dish aside, well covered, and allow to cool. When cold, add the spirit of orange, the sugar, and enough distilled water to make the whole weigh 1,000 Gm. When the sugar has been dissolved by stirring, strain the syrup through loose cotton placed in the neck of the funnel, which is to be kept covered, and transfer the filtered syrup to small vials, which should be completely filled, securely corked, and kept in a cool and dark place.

Reaction.— $2\text{I}_2 + 2\text{H}_2\text{S} = 4\text{HI} + \text{S}_2$.

Notes.—The reaction is aided by having the iodine finely divided, as will be the case when it is dissolved in alcohol and the solution then shaken with syrup and water. The hydriodic acid first formed dissolves more iodine, which also aids the reaction. As the sulphur precipitates, however, it may so envelop the undissolved portion of the iodine that the hydrogen sulphide does not come into contact with it. The iodine ought, therefore, to be added in small portions at a time, and the mixture should be frequently well stirred, breaking up the deposit of sulphur, and distributing the undissolved iodine through the liquid as far as practicable.

Description.—A colorless, or nearly colorless, liquid, with a sweetish acid taste.

Tests.—Starch paste added to the liquid should not strike a blue color, showing absence of free iodine. A slight bluish tinge would indicate a trace of iodine.

Barium chloride solution should not produce a precipitate of sulphate.

The specific gravity of the syrup should be 1.300.

25.5 Gm. should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

IODIDE OF SULPHUR.**SULPHURIS IODIDUM.**

Washed sulphur 1 part.
 Iodine 4 parts.

Rub them together until thoroughly mixed. Introduce the mixture into a small bottle, close the orifice loosely, and apply a gentle heat by water-bath so as to darken the mass without melting it. When the color has become uniformly dark throughout, increase the heat so as to produce liquefaction, and incline the bottle in different directions, in order to return into the liquid any portion of iodine which may have been condensed on the inner surface. Then withdraw the heat, and, after the liquid has become solid, break the bottle, reduce the fused mass to pieces, and keep it in a glass stoppered bottle.

Description.—A dark gray crystalline solid having the composition I_2S_2 . Melts at about $60^\circ C.$, and is insoluble in water. Dissolves in carbon disulphide. Gradually decomposes in the air, giving off odor of iodine.

Tests.—Treated with alcohol it is decomposed, the iodine being dissolved and the sulphur deposited.

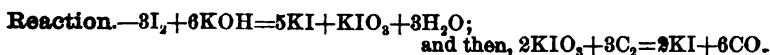
Boiling water decomposes it slowly, and if the heat be continued long enough the iodine can be entirely driven off.

POTASSIUM IODIDE.**POTASSII IODIDUM.**

$KI = 165.6.$

Solution of potassa 1,000 C.c.
 Iodine 100 Gm., or sufficient.
 Wood charcoal, in fine powder 15 Gm.
 Boiling distilled water, sufficient.

Put the solution of potassa in a flask, add the iodine, a little at a time, with constant agitation, until the solution becomes permanently brown. Evaporate to dryness. Powder the residue, and mix it well with the charcoal. Throw the mixture into a red-hot iron crucible, and when the whole is in a fused condition pour it out to cool, dissolve it in 200 C.c. of boiling distilled water, filter, and evaporate until a pellicle forms. Then set aside to cool and crystallize. Drain the crystals and dry them in a warm place. The remainder of the salt may be obtained from the mother liquor by evaporation to dryness, stirring constantly.



Notes.—The red brown liquid formed by dissolving iodine in solution of potassa contains potassium iodide and potassium iodate, as seen from the above equation. By heating the salt mass obtained on evaporation of this liquid to dryness, the iodate is reduced to iodide; but the heat necessary for this purpose is so high that loss of iodine ensues, and the product becomes alkaline. To prevent this, charcoal is added, which makes the reduction practicable at a much lower temperature.

The crystallization of potassium iodide is somewhat difficult. It is best to continue the evaporation until a sample of the liquid, when removed from the vessel, crystallizes on cooling. The liquid should then be left in a warm place (50° to 60° C. = 122° to 140° F.), where the evaporation may continue spontaneously in order that large crystals may be obtained. At a lower temperature the iodide ascends the sides of the vessel and creeps over the edges.

When perfectly pure, potassium iodide is difficult to obtain in colorless crystals; it undergoes partial decomposition with liberation of enough iodine to discolor the product. To prevent this discoloration the liquid is usually rendered slightly alkaline before being set aside for crystallization. The presence of potassium carbonate not only facilitates the formation of crystals, but also renders the product whiter. The Pharmacopœial tests permit a slight alkalinity (less than 0.1 per cent.). Crystals of perfectly pure potassium iodide are usually not quite white, but may be made so by drying at 120° to 125° C. (248° to 257° F.).

Potassium iodide is also prepared as follows:

Iron wire, cut.....	60 Gm.
Iodine	200 Gm.
Potassium bicarbonate	160 Gm.
Distilled water, sufficient.	

Digest the iron and 150 Gm. of the iodine with 500 C.c. of water in a flask until all odor of iodine ceases and a green solution of ferrous iodide results. Filter this, and in the filtrate dissolve the remainder of the iodine.

Put the potassium bicarbonate into a dish with 800 C.c. of distilled water, heat until effervescence ceases, and then raise the heat to boiling. Add slowly to this boiling hot solution the filtered solution of the iodides or iron. Boil the mixture for fifteen minutes. (If all the iron has not been precipitated from the solution, add a little more potassium bicarbonate.) Filter, evaporate, and crystallize.



Notes.—As seen from the equation, a solution of ferrous iodide is first made. This can be at once treated with potassium carbonate to obtain the potassium iodide: $\text{FeI}_2 + \text{K}_2\text{CO}_3 = \text{FeO} + 2\text{KI} + \text{CO}_2$. But in this case the iron is separated with greater difficulty, being first thrown down as ferrous carbonate, which at once begins to lose carbonic acid, and at the same time oxidizes so that the precipitate gradually changes from light gray to blue, yellowish brown, and finally to brown ferric hydrate ($\text{Fe}_2(\text{OH})_6$). All of the iron does not separate at once, however, so that during the subsequent evaporation of the filtered solution of iodide of potassium a considerable quantity of flocculent deposit of ferric hydrate makes its appearance and must be filtered out.

This difficulty may be remedied to a great extent by converting the ferrous iodide into ferrico-ferrous iodide by adding the required additional quantity of iodine. The precipitate will then, after the boiling, be black magnetic oxide of iron, which is very dense and, therefore, more easily separated than ferric hydrate.

Description.—Colorless, translucent or opaque cubical crystals, very soluble in water and soluble in alcohol.

The salt can be melted at a high temperature, but not without slight decomposition.

Tests.—The solution of the pure salt should have a neutral reaction, but a slight alkalinity is usually observed.

The aqueous solution treated with starch paste and dilute sulphuric acid should not show a blue color immediately, showing absence of iodate.

The aqueous solution should show no precipitate, and not more than a slight opalescence when treated with solution of barium nitrate.

.3312 Gm. of the dry salt should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

Composition.—Potassium iodide contains 76.45 per cent. of iodine.

Uses.—In pharmaceutical chemistry it is employed for the preparation of various other iodides, as those of ammonium, mercury, lead, silver, etc.

Specific Gravity and Percentage Strength of Solutions of KI.

(Schiff.)

Per cent. of KI.	Sp. gr. 21°.
10	1.0793
20	1.1705
30	1.2784
40	1.4079
50	1.5640
60	1.7517

SODIUM IODIDE.

SODII IODIDUM.



Iron wire, cut 60 Gm.
 Iodine 200 Gm.
 Sodium carbonate 240 Gm.
 Distilled water, sufficient.

Digest the iron and 150 Gm. of the iodine with 500 C.c. of water in a flask until the odor of iodine ceases and a green solution of ferrous iodide results. Filter this, and dissolve the remainder of the iodine in the filtrate. Dissolve the sodium carbonate in 800 C.c. of water, heat to boiling, then add the solution of iodides of iron during constant stirring, boil the mixture fifteen minutes, filter, evaporate, and crystallize.

Notes.—The reactions are analogous to those taking place in the process for preparing potassium iodide in a similar way. See also the notes under that title.

Sodium iodide may also be made from iodine and solution of soda, as potassium iodide is prepared from iodine and solution of potassa.

Description.—Powder, or small cubical crystals, very readily soluble in water and alcohol.

Melts at a low red heat, and volatilizes with slight decomposition.

Tests.—Similar to those for potassium iodide.

.2992 Gm. of the dry salt should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for complete precipitation.

LITHIUM IODIDE.

LITHII IODIDUM.

$$\text{LiI} = 133.6.$$

Prepared by double decomposition between calcium iodide and lithium carbonate, which are heated together in water. $\text{CaI}_2 + \text{Li}_2\text{CO}_3 = 2\text{LiI} + \text{CaCO}_3$. It may also be made from iron, iodine and lithium carbonate, in a manner similar to the process for preparing bromide of lithium from iron, bromine and lithium carbonate.

AMMONIUM IODIDE.

AMMONII IODIDUM.

$$\text{NH}_4\text{I} = 144.6.$$

Potassium iodide.....	64 Gm.
Ammonium sulphate.....	29 Gm.
Boiling distilled water.....	30 C.c.
Alcohol, sufficient.	

Powder and mix the salts, add the boiling water, stir well, and then allow the mixture to slowly cool. Then add 80 C.c. of alcohol, mix thoroughly, and set the vessel containing the mixture in an ice-water bath, stirring occasionally. When cooled to about 5° C. (41° F.) throw the mixture into a cool glass funnel having a loose plug of moist cotton placed in its throat. Collect the clear filtrate and evaporate it to granulation. The product should be at once put in a bottle, which must be tightly corked.

Reaction.— $2\text{KI} + (\text{NH}_4)_2\text{SO}_4 = 2\text{NH}_4\text{I} + \text{K}_2\text{SO}_4$.

Notes.—This process is based upon the solubility of ammonium iodide and the insolubility of potassium sulphate in dilute alcohol.

Ammonium iodide is an unstable salt, soon turning yellow or even brown from free iodine. Discolored ammonium iodide may be restored, as suggested in the Pharmacopœia, by washing with ether and rapidly drying. In order to be fit for use this salt should be white and inodorous.

Description.—A white granular salt, turning yellow or brown as above described. Very soluble in water. Volatilizes with decomposition.

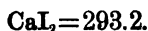
Tests.—Should be completely soluble in water; the solution mixed with starch paste should not show more than a slight blue tinge from free iodine.

Complete volatility indicates absence of fixed compounds.

.2892 Gm. of the dry salt should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for complete precipitation.

CALCIUM IODIDE.

CALCII IODIDUM.



Iodine	20 parts.
Iron	8 parts.
Lime	5 parts.
Water, sufficient.	

Digest the iron and 15 parts of the iodine with 30 parts of water, in a flask, until all odor of iodine ceases and a green solution of ferrous iodide is obtained. Filter this, then add the remainder of the iodine, and dissolve.

Slake the lime with 6 parts of water, and triturate the calcium hydrate with enough water to make a smooth liquid mixture. Add this milk of lime gradually to the solution of iron iodides until the iron has all been precipitated. Then filter the liquid and evaporate it to dryness, stirring constantly.

Reactions.— $\text{Fe}_3 + 2\text{I}_2 = 2\text{FeI}_2$; then, $2\text{FeI}_2 + \text{I}_2 = \text{Fe}_2\text{I}_4$;
then, $\text{Fe}_2\text{I}_4 + 3\text{CaO} = 3\text{CaI}_2 + \text{Fe}_2\text{O}_3$.

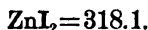
Description.—Obtained above as a white granular mass. It can be crystallized in pearly scales. The salt is soluble in water and alcohol, but the solutions are not permanent.

Tests.—The usual tests should show absence of sulphates, etc. The tests for chlorides and bromides are best carried out by the method given for the separation of the three halogens under Qualitative Analysis.

.2932 Gm. should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

ZINC IODIDE.

ZINCI IODIDUM.



Granulated zinc	30 Gm.
Iodine	100 Gm.
Distilled water	200 C.c.

Digest together in a flask until colorless and free from the odor of iodine. Filter through asbestos or powdered glass, and evaporate the filtrate rapidly to dryness at a moderate heat.

Must be kept in small well closed vials.

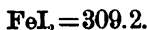
Description.—A white granular salt, very readily soluble in water and alcohol.

Tests.—Complete solubility in water. If the solution is made alkaline by ammonia water and treated with excess of ammonium sulphide, the whole of the zinc is thrown down as a *white* precipitate. The liquid filtered from this should give no precipitate with solution of ammonium carbonate.

.3181 Gm. of the dry salt should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation.

FERROUS IODIDE.

FERRI IODIDUM.



Iron wire, cut	60 Gm.
Iodine	170 Gm.
Distilled water	200 C.c.

Digest in a flask at a moderate heat until all odor of iodine has ceased and a green solution has been obtained. Filter the solution and evaporate the filtrate as rapidly as possible in a polished iron dish until a trial drop solidifies on cooling. Then pour the liquid out on a porcelain slab, and as soon as it has hardened break it into pieces while still warm, and put it into small, dry, warm bottles, which must be at once tightly stoppered.

For reaction and notes see Syrup of Ferrous Iodide.

Description.—As commonly made a greenish brown unstable salt, which slowly decomposes in presence of moisture.

The above process gives a grayish mass, which is not completely soluble in water, a little oxide usually remaining.

Tests.—3092 Gm. should require 20 C.c. of $\frac{N}{10}$ silver nitrate solution for precipitation when pure.

SACCHARATED FERROUS IODIDE.

FERRI IODIDUM SACCHARATUM.

Iron, in the form of fine wire, and cut into small pieces	6 parts.
Iodine	17 parts.
Distilled water	20 parts.
Sugar of milk	80 parts.

Mix the iron, iodine, and distilled water in a flask, shake the mixture occasionally until the reaction ceases, and the solution has acquired a green color and lost the odor of iodine; then filter it through a wetted filter into a porcelain dish containing 40 parts of sugar of milk. Rinse the flask and iron wire with a little distilled water, pass the rinsings through the filter into the dish, and evaporate, on a water-bath, constantly stirring until dry. Transfer the mass quickly to a heated iron mortar containing the remainder of the sugar of milk, and reduce the whole to powder.

Transfer the powder at once to small, well-dried bottles, which must be securely stoppered, and kept in a cool and dark place.

Notes.—By intermixture with sugar of milk the ferrous iodide is in some measure protected from oxidation.

The Pharmacopœial description and tests are as follows:

A yellowish-white or grayish powder, very hygroscopic, odorless, having a sweetish, ferruginous taste, and a slightly acid reaction. Soluble in 7 parts of water at 15° C. (59° F.), forming an almost clear solution; only partially soluble in alcohol. When strongly heated, the compound swells up, chars, evolves the odor of iodine and of burnt sugar, and, on ignition, leaves a residue which should yield nothing soluble to water (abs. of salts of alkalies). The aqueous solution yields a blue precipitate with test-solution of ferricyanide of potassium. If mixed with some gelatinized starch and afterward with a little chlorine water, the solution assumes a deep blue color. This color should not be developed in the aqueous solution by gelatinized starch alone (abs. of free iodine).

On mixing an aqueous solution of 5 Gm. of saccharated iodide of iron with a solution of 1 Gm. of nitrate of silver, and filtering, the filtrate should still produce a precipitate of cloudiness with test-solution of nitrate of silver (presence of at least 20 per cent. of ferrous iodide).

SYRUP OF IODIDE OF IRON.

SYRUPUS FERRI IODIDI.

A syrupy liquid containing 10 per cent. of ferrous iodide (FeI_2 , 309.2).

Iron, in the form of fine wire, and cut into small pieces.....	25 Gm.
Iodine.....	82 Gm.
Sugar, in coarse powder.....	600 Gm.
Distilled water, sufficient.	

Introduce the iron into a flask, add 200 C.c. of distilled water, and afterward the iodine. Shake the mixture occasionally, until the reaction ceases and the solution has acquired a green color and has lost the odor of iodine. Place the sugar in a porcelain dish and filter the solution of iodide of iron into the sugar. Rinse the flask and iron wire with 90 C.c. of distilled water, and pass the washings through the filter into the sugar. Stir the mixture with a glass rod, heat it to the boiling point

on a sand-bath, and having filtered the syrup through white paper into a tared bottle, add enough distilled water to make the product weigh 1,000 Gm. Lastly, shake the bottle, which should be completely filled and securely stoppered.

Reaction.— $\text{Fe}_2 + 2\text{I}_2 = \text{FeI}_2$.

Notes.—The proportion of iron combining with 8.20 parts of iodine to form ferrous iodide is only a little over 1.80 parts, so that the iron is present in large excess. This is to facilitate the complete saturation of the iodine. At first the reaction is tardy, and may require the aid of heat to start it; but as soon as some ferric and ferrous iodide have been formed the iodine dissolves in their solution, and after that the iodine acts rapidly on the iron with the evolution of heat. If this elevation of temperature is too great there will be a loss of iodine by vaporization. The heat must not be so great that violet vapors of iodine fill the flask. It is safest to add the iodine in small portions at a time, during brisk stirring, allowing the liquid to become green instead of red-brown after each addition before adding more.

The reaction between iron and iodine will take place at all temperatures, but is slow in cold. Should the reaction proceed at a comparatively low temperature until all the iodine has been added, and cease without leaving a liquid of bright green color when filtered, the application of heat before removing the undissolved iron will always bring out the green color, which is the sign of completed reaction.

To prevent oxidization the solution of ferrous iodide should be filtered as rapidly as possible and while still hot, directly into the sugar.

Success in preparing a perfect syrup of iodide of iron depends upon a perfectly completed reaction, careful control of the temperature so that no iodine shall be lost, the use of pure distilled water and pure white sugar, and scrupulous cleanliness in regard to the vessels and implements used. The Pharmacopœia is in error in suggesting the use of a "wooden spatula."

Syrup of iodide of iron may be successfully preserved in corked bottles, but with much less risk in glass stoppered bottles. Exposure to light seems to decolorize the preparation, even after the green color has changed to a pale yellowish. But in order to best preserve a bright green syrup of ferrous iodide from change it should be kept in a shaded, though not dark place.

Unless the bottle containing the syrup is filled, the surface of the preparation soon becomes yellow or yellowish brown from oxidization by contact with the air above it. Hence the direction that the bottle shall be filled.

When this preparation becomes slightly discolored—yellowish green but not yellow or yellowish brown—the bright green color can usually be restored by heating it to near the boiling point in a flask by means of a water-bath.

Straining as directed in the Pharmacopœia will not suffice to make the product clear. It must be filtered through white filter-paper.

As the preparation is prone to discoloration by decomposition, assuming a yellowish brown color from free iodine, various means have been suggested to prevent this change. It was at one time proposed to place a piece of polished iron—for example, a nail filed until bright over its whole surface—in the syrup; but this is worse than useless. Another and more successful plan was to add tartaric or citric acid, in the proportion of about 1 part in 500. All such additions are, however, unnecessary, as the preparation will keep well if properly made and put into clean, glass stoppered bottles in the manner indicated above.

Glycerite of ferrous iodide is a perfectly stable preparation, and ought, therefore, to be used in preference to the syrup.

The Pharmacopœial description and tests are as follows:

A transparent, pale green liquid, odorless, having a sweet, strongly ferruginous taste, and a neutral reaction. With test-solution of ferricyanide of potassium it yields a blue precipitate. If a little disulphide of carbon be added to the syrup, then a few drops of chlorine water, and the whole agitated, the disulphide will separate with a purple or violet color. It should not deposit a sediment on keeping, and should not tinge gelatinized starch blue (abs. of free iodine).

10 Gm. of the syrup should require for complete precipitation not less than 1.09 Gm. of nitrate of silver (corresponding to 10 per cent. of ferrous iodide).

GLYCERITE OF FERROUS IODIDE.**GLYCERITUM FERRI IODIDI.**

Iodine.....	82 Gm.
Iron wire.....	80 Gm.
Distilled water.....	150 C.c.
Glycerin.....	300 C.c.

Digest the iron wire and iodine together in the water, contained in a flask, until the liquid has acquired a bright green color, and lost all odor of iodine. Filter the solution into the glycerin, mix well, and evaporate the mixture until it weighs 500 Gm.

Notes.—This glycerite keeps indefinitely, mixes clear with water, alcohol, and syrup, and is exactly twice the strength (in ferrous iodide) of the Pharmacopœial syrup of iodide of iron (U. S.).

SYRUP OF MANGANOUS IODIDE.**SYRUPUS MANGANI IODIDI.**

Manganous sulphate.....	40 Gm.
Potassium iodide.....	50 Gm.
Sugar.....	280 Gm.
Simple syrup, distilled water, each sufficient.	

Dissolve each of the salts in 50 C.c. of water mixed with 10 C.c. of simple syrup. Mix the solutions and shake well. Cool the mixture to about 10° C. (50° F.). Filter, rinsing the precipitate on the filter with a little sweetened water, letting the filtrate and washings run into a bottle containing the sugar. Shake until dissolved, and then add enough distilled water to make the total product measure 400 cubic-centimeters.

Reaction.— $\text{MnSO}_4 + 2\text{KI} = \text{K}_2\text{SO}_4 + \text{MnI}_2$.

Notes.—The manganous iodide is very deliquescent and prone to rapid decomposition. Hence it is not used except preserved by sugar in the form of syrup.

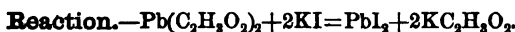
The application of cold in the process is to cause the separation of the potassium sulphate as far as possible.

LEAD IODIDE.**PLUMBI IODIDUM.**

$\text{PbI}_2 = 459.7$.

Lead acetate.....	9 parts.
Potassium iodide.....	8 parts.
Acetic acid.....	1 part.

Dissolve the acetate in 90 parts of cold water, add the acid, and filter. Dissolve the iodide in 80 parts of cold water and filter. Pour the lead salt solution into the solution of potassium iodide, stirring constantly. Set aside to settle. Decant the mother liquor and throw it away. Collect the precipitate on a filter and wash it with cold water. Dry it between bibulous paper.



Notes.—The addition of acetic acid to the solution of lead acetate is to prevent the precipitation of white carbonate and yellowish white oxyiodide of lead. Lead iodide is not more soluble in acetic acid than it is in water. Cold solutions are used not only because lead iodide is soluble to a considerable extent in hot water, but also to obtain a more finely divided product. When hot liquids are used a portion of the iodide is held in solution until the liquid is cold, separating gradually in crystalline scales. Lead iodide is also soluble in cold water, and thus there is always a slight loss, which is increased by washing. Hence the quantity of water used for washing the precipitate should be limited, and the washing should be performed on a filter instead of by decantation.

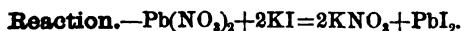
The lead acetate solution must be added to the solution of the iodide, for it is necessary to have the latter present in excess until the liquids are mixed. Should the order of mixing be reversed, or should the lead acetate be in excess, oxyiodide of lead is formed. On the other hand, if the potassium iodide is in too great excess after all the lead acetate has been added, loss will be occasioned by the formation of soluble double salts of the iodides of lead and potassium. Potassium acetate also dissolves lead iodide. To obtain a larger yield, lead nitrate is used instead of acetate, the lead iodide being almost insoluble in a solution of potassium nitrate. The formula is then as follows:

SECOND METHOD.

Lead nitrate	1 part.
Potassium iodide	1 part.
Water, sufficient.	

Dissolve the lead nitrate in 8 parts of cold water, and the potassium iodide in 3 parts of cold water. Filter the solutions. Add the lead solution to the solution of potassium iodide, with stirring. Decant the mother liquor and throw it away. Collect the precipitate on a filter and wash it with cold water. Dry it between bibulous paper.

(If a crystalline product is desired, dissolve the washed and still wet precipitate by boiling it with two hundred times its weight of water, filter, and let the solution cool very slowly. The lead iodide obtained from 10 Gm. of lead nitrate would require nearly three liters of boiling water for its solution. To obtain a small quantity of crystallized lead iodide as a specimen, boil the precipitate with 200 times its weight of water, filter while hot, and set the filtrate aside to cool slowly. The undissolved portion should be reserved separately.)

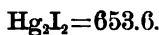


Description.—A lemon yellow powder permanent in the air. Becomes yellowish red and then red on heating. It is soluble in about 1,500 parts of cold water.

Tests.—Should be completely soluble in solution of ammonium chloride. Dilute sulphuric acid precipitates all the lead from this, and the clear supernatant liquid should not give tests for other substances.

MERCUROUS IODIDE.

HYDRARGYRI IODIDUM VIRIDE.



Mercury.....	8 parts.
Iodine.....	5 parts.
Alcohol, sufficient.	

Pour the mercury into a mortar; add 3 parts of alcohol; then add the iodine, and triturate all together. When the alcohol has nearly evaporated, add a little more, from time to time, so as to keep the mixture moist. This is done in order to prevent the temperature from rising too high from the heat generated by the chemical union between the mercury and iodine. Continue the trituration until all globules of mercury have disappeared, and the mixture, when nearly dry, has acquired a greenish yellow color.

Now add sufficient alcohol to reduce the whole to a thin paste, pour this into a wide-mouthed bottle, cork it well, and set it aside in a dark place for several days.

Then pour off the alcohol, and add in its place 50 parts of warm alcohol, shake well, and again set it aside for a day or two. Decant again, and once more wash the mercurous iodide with 50 parts of warm alcohol. Shake the mixture well, transfer it to a white paper filter, and continue washing the precipitate with alcohol until the washings are no longer affected by hydrogen sulphide.

When the washing has been completed as described, dry the product between white filter-paper in a dark place at a temperature not exceeding 40° C. (104° F.).

Keep the product in a well closed bottle protected from light.

Reaction.— $\text{Hg}_2 + \text{I}_2 = \text{Hg}_2\text{I}_2$.

Notes.—The alcohol washes out the mercuric iodide, a small quantity of which is always formed simultaneously with the mercurous iodide, the former being soluble but the latter insoluble in alcohol.

As seen in the trade and the shops this preparation varies from bright greenish yellow to dark grayish green. Exposure to air while in a moist condition is said to affect the color. Light decomposes mercurous iodide into metallic mercury and mercuric iodide, and the green hue of the preparation probably arises from

the blending of the bluish metal with the yellow mercurous iodide. The darker its color the greater are the amounts of mercury and of mercuric iodide contained in the preparation. Hence a dark colored "mercurous iodide" is unfit for use, the mercuric iodide it contains being poisonous.

Description.—Nearly insoluble in water. When washed with alcohol the washings should not leave more than traces of a residue on evaporation.

MERCURIC IODIDE.

HYDRARGYRI IODIDUM RUBRUM.

HgI_2 —453.2.

Mercuric chloride, in powder..... 12 parts.

Potassium iodide..... 15 parts.

Dissolve the mercuric chloride in 200 parts of hot distilled water, and filter. Dissolve the potassium iodide in 40 parts of cold distilled water, and filter. Pour the solution of mercuric chloride when cold into the solution of potassium iodide, stirring constantly. Set aside until the precipitate has subsided perfectly. Decant the mother liquor and set it aside. Wash the precipitate with 300 parts of cold water, stirring it up well, allowing it to subside again, and at once decanting the washings. Then collect the precipitate upon a white paper filter, and continue washing with distilled water until the washings cease to give a precipitate with test-solution of silver nitrate. Dry the iodide between white filter paper at a temperature not exceeding 40°C . (104°F). Keep it in well closed bottles.

Reaction.— $\text{HgCl}_2 + 2\text{KI} = \text{HgI}_2 + 2\text{KCl}$.

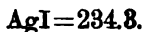
Notes.—The proportions here given are to be preferred to those given in the U. S. Pharmacopœia, which are 9 to 11. Theoretically we should require for 12 parts of mercuric chloride about 14.7 parts of potassium iodide; but the potassium iodide generally contains small quantities of carbonate and other impurities, and it is moreover desirable to use a slight excess of the potassium iodide, to prevent the formation of a light-red compound of mercuric chloride with mercuric iodide. For this reason, also, the solution of mercuric chloride must be poured into that of the potassium iodide so as to keep the latter at all stages of the process in excess over the mercuric chloride with which it is being mixed, and constant stirring is directed with the same object in view.

Unless the solutions are filtered before mixing them, the product, besides retaining mechanical impurities, may possibly also contain mercurous chloride, the mercuric chloride being frequently contaminated with it.

Crystallized mercuric iodide.—Use the same materials and in the same proportions as given above, but use hot solutions. The mercuric iodide being soluble in a hot solution of potassium chloride, the product crystallizes in the gradual cooling. The yield is about 20 parts.

Description.—A beautiful scarlet red crystalline powder, insoluble in water, but soluble in solution of potassium iodide or of mercuric chloride. Completely volatile by heat.

Tests.—The water washings should leave not more than a trace of residue on evaporation.

SILVER IODIDE.**ARGENTI IODIDUM.**

Silver nitrate.....	1 part.
Potassium iodide.....	1 part.

Dissolve the salts separately, each in about 12 parts of distilled water. Pour the solution of silver nitrate gradually and with constant stirring into the solution of the iodide. Collect the precipitate on a filter, wash it well with distilled water, and dry it between bibulous paper.

Reaction.— $\text{AgNO}_3 + \text{KI} = \text{AgI} + \text{KNO}_3$.

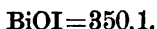
The product is to be kept in well closed bottles and protected from light.

Description.—A heavy light yellow powder, insoluble in water, which melts to a deep red liquid when strongly heated.

It is easily soluble in solution of potassium cyanide, and but *very slightly* in strong ammonia water.

Tests.—If washed with water this should leave not more than a *slight* trace of residue on evaporation.

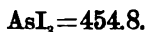
If washed with ammonia water this should not become more than very slightly opalescent when treated with an excess of pure nitric acid.

OXY-IODIDE OF BISMUTH.**BISMUTHI OXY-IODIDUM.**

Bismuth subnitrate.....	12 parts.
Potassium iodide.....	7 parts.
Distilled water.....	15 parts.

Mix and digest together in a bottle for an hour, shaking occasionally. Then transfer to a filter, and wash with warm water until the washings are tasteless. Drain, and dry between filter-paper.

Reaction.— $\text{BiONO}_3 \cdot \text{H}_2\text{O} + \text{KI} = \text{KNO}_3 + \text{BiOI} + \text{H}_2\text{O}$.

IODIDE OF ARSENIC.**ARSENI IODIDUM.**

Arsenic.....	3 parts.
Iodine.....	16 parts.

Triturate until finely powdered and thoroughly mixed. Put it into a flask and heat gently on a water-bath, inclining the flask in different directions, until fusion takes place. Pour the fused mass upon a porcelain slab and let it cool, then break it into pieces and keep it in well stoppered bottles in a cool place.

Description.—Dark orange red crystalline masses, having the odor of iodine. Water soluble.

SOLUTION OF IODIDE OF ARSENIC AND MERCURY.

LIQUOR ARSENI ET HYDRARGYRI IODIDI.

Iodide of arsenic	1 part.
Red iodide of mercury	1 part.
Distilled water, sufficient.	

Triturate the iodides with 15 parts of distilled water, until dissolved. Filter the liquid and pass enough distilled water through the filter to make the product weigh 100 parts.

Notes.—No chemical reaction takes place in dissolving the two iodides together; but the mercuric iodide is soluble in the solution of arsenous iodide, although almost insoluble in water.

CHAPTER XIV.

CYANIDES.

The cyanides of potassium and mercury are water soluble; the others described in this work are insoluble in water. All may be prepared with hydrocyanic acid except the ferrocyanide of iron. Potassium cyanide may also be prepared by heating a mixture of potassium ferrocyanide and potassium carbonate.

DILUTED HYDROCYANIC ACID.

ACIDUM HYDROCYANICUM DILUTUM.

[PRUSSIC ACID.]

 $\text{HCy} = 27.$

Contains 2 per cent. of hydrogen cyanide. The Pharmacopoeial diluted hydrocyanic acid of the United States is a solution of the acid in water mixed with alcohol.

Potassium ferrocyanide, in coarse powder..... 4 parts.
Sulphuric acid..... 3 parts.

The apparatus necessary consists of a long-necked flask fitted with a twice perforated stopper carrying a safety tube and the bent tube connecting the flask with a Liebig's or other suitable condenser, the exit tube of which should dip into the liquor in the receiver. The receiver should be tared, should be large enough to permit the final adjustment of strength without a change of vessel, and should be placed in broken ice or ice water.

Put 16 parts of distilled water in the receiver.

The ferrocyanide is to be dissolved in 20 parts of water and then introduced into the flask. The acid is diluted by adding it gradually to twice its weight of water, and, after connecting the whole apparatus together properly and making all the joints tight, the cold diluted acid is poured in through the safety tube. Heat the flask on a sand-bath to the boiling point, and continue applying a moderate heat until there is but little liquid mixed with the saline mass remaining in the flask. Then detach the receiver and dilute its contents with distilled water so that the product shall contain just 2 per cent. of absolute hydrocyanic acid.

Reaction.— $2K_2FeCy_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe_2Cy_6 + 6HCy$. (The ferrocyanide of iron and potassium contained in the residue is called "Everitt's salt.")

Notes.—The process here given is nearly identical with that of the U. S. Pharmacopœia of 1870. A flask has been substituted for a retort because more convenient, and to prevent the contamination of the product with the contents of the generator from spurting.

In the process of the present U. S. Pharmacopœia (1882) the receiver is to contain 12 parts of diluted alcohol instead of 16 parts of water; the ferrocyanide is directed to be put into the retort with only twice its weight of water, and the acid to be diluted with only an equal weight of water. The utility of these modifications is doubted by good authority.

The object of using dilute alcohol to absorb the gas is to promote the stability of the product; but it is doubtful whether this end is gained.

The heat required is not far above the boiling point of water. A sand-bath is to be preferred to naked flame to avoid bumping. The reaction should be slow and regular, which requires rather diluted solutions, as here indicated, and sufficient control of the heat. But too great dilution favors bumping.

When the process is carried out as directed in the formula above stated, the distillate will contain about 8 to 4 per cent. of hydrocyanic acid.

Adjustment of strength.—Dr. Squibb recommends the following method: In a beaker of the capacity of 100 C.c. put 50 C.c. of distilled water, 5 C.c. of the official solution of potassa (10 per cent.), and two or three drops of a cold saturated solution of sodium chloride. Stir the mixture with a small glass rod, and take the total weight of beaker, contents, and stirrer. Then introduce into it, by means of a pipette, 2.50 C.c. of the strong hydrocyanic acid from the receiver, letting the point of the pipette just touch the surface of the liquid in the beaker so that the stream delivered from the pipette may not be exposed to contact with the air. The pipette, however, should not dip more than a millimeter below the surface of the liquid, to avoid undue loss of liquid by adhesion to the pipette when removed. Stir the mixture gently, and again weigh the beaker and contents. The difference of this weight and that first taken is the weight of the hydrocyanic acid added. Now run in, from a burette, just enough decinormal solution of silver nitrate to produce a slight but permanent turbidity or opalescence in the liquid. Then read off the quantity of silver nitrate solution used. Each C.c. of the silver solution used is equal to .0054 Gm. of absolute hydrocyanic acid. Therefore, .0054 multiplied by the number of C.c. of silver solution used represents the total quantity of absolute hydrocyanic acid contained in the 2.50 C.c. of strong distillate taken for the assay. The weight of that 2.50 C.c. of distillate is to its total contents of HCy as 100 is to the percentage. Thus if the 2.50 C.c. of distillate taken for the assay weighed 2.42 Gm., and if the quantity of silver solution used was 22 C.c., then:

2.42 : 1188 :: 100 : x, and x equals 4.909+ per cent.

The receiver having been already tared, the weight of its contents is now ascertained. This weight multiplied by 0.04909 gives the total contents of absolute hydrocyanic acid in the strong distillate which is to be diluted, and enough distilled water is then added to make the total product weigh 50 times the weight of the total absolute hydrocyanic acid found in the distillate.

The product should be subjected to a repetition of the process of assay for the purpose of verification.

The method of assay here described is Liebig's. That of the Pharmacopœia is more liable to error, and not superior in any respect.

Diluted hydrocyanic acid always sustains loss of hydrogen cyanide in handling it. This weakening of the acid is appreciable in filling it in small bottles, and as it must be kept in small bottles, to avoid too great and frequent exposure to air in using, it may be well to make the product about 2.1 instead of 2 per cent. strength to insure that the bottled acid may be slightly above 2 per cent. immediately after bottling, and not much below 2 per cent. before consumed in dispensing. (Squibb.)

Preservation.—Diluted hydrocyanic acid loses strength by long keeping. It also frequently undergoes some change by which a dark colored deposit is formed in it. According to Squibb, it may turn "nearly as black as dilute ink" within a year and a half, *if kept in glass stoppered bottles*, and this change does *not* occur when the acid is put up in corked vials. The action which the acid thus appears to have upon the ground surface of glass has not been explained.

The preparation should always be kept in a cool, dark place.

OFFICIAL ALTERNATE PROCESS.

The Pharmacopœia also gives an easily performed process for the extemporaneous preparation of diluted hydrocyanic acid, which is as follows:

Silver cyanide	6 parts.
Hydrochloric acid	5 parts.
Distilled water	55 parts.

Mix these ingredients in a glass stoppered bottle, adding the cyanide last, and shake well. When the precipitate has subsided, pour off the clear liquid, which will be the finished product, containing 2 per cent. of HCy.

Reaction.— $\text{AgCy} + \text{HCl} = \text{AgCl} + \text{HCy}$.

Description.—A colorless volatile liquid, recognized by its odor of bitter almonds.

POTASSIUM CYANIDE.

POTASSII CYANIDUM.

KCy=65.

Potassium ferrocyanide, dried and powdered, ...	8 parts.
Potassium carbonate, dry	3 parts.

Mix the powdered materials well, throw the mixture into a deep iron crucible previously heated to dull redness, and maintain the heat until effervescence ceases and the fused mass solidifies on cooling, which may be ascertained by dipping a warm glass rod in it and withdrawing. When the fused cyanide assumes a pure white color on cooling, pour it out into a shallow dish, and, when solid, break it into pieces and put it up while still warm.

Reaction.— $2K_4FeCy_6 + 2K_2CO_3 = 10KCy + 2KOCy + 2CO_2 + Fe_2$.

Notes.—Care is to be taken to decant the fused cyanide properly from the residue—that is, the pouring must be discontinued as soon as the decanted fused salt is no longer white.

The product contains cyanate as well as cyanide.

Another process consists in conducting hydrocyanic acid into solution of potassa to which alcohol has been added. The cyanide formed is then deposited in small crystals, which are to be drained on a funnel, washed with strong alcohol, in which the preparation is nearly insoluble, and dried between bibulous paper at a moderate heat.

Being deliquescent, and readily absorbing carbonic acid from the air with the formation and loss of hydrocyanic acid, the product must be kept in tightly closed bottles.

Description.—An opaque white solid, very soluble in water, possessing the peculiar odor of prussic acid. This odor is not observed in the perfectly pure dry salt which has not been exposed to the carbonic acid of the air.

In moist air CO_2 displaces Cy, and the salt in this way becomes contaminated by potassium carbonate.

Tests.—When the solid is dissolved in water and standard solution of silver nitrate is added, a permanent precipitate does not form until half of the salt has combined with silver.

20 C.c. of $\frac{N}{10}$ silver nitrate solution are equivalent to .2600 Gm. of the pure substance.

Very little of the commercial article possesses the purity (90 per cent.) required by the Pharmacopœia.

ZINC CYANIDE.

ZINCI CYANIDUM.

$ZnCy_2 = 116.9$.

Prepared by precipitating a solution of zinc acetate with hydrocyanic acid.

Description.—A colorless salt insoluble in water and alcohol, but soluble in solutions of alkalis, with which it forms double cyanides.

FERROCYANIDE OF IRON.

FERRI FERROCYANIDUM.

$Fe_4(FeCy_6)_3 = 860$.

Solution of ferric chloride 230 C.c.

Ferrocyanide of potassium 140 Gm.

Distilled water, sufficient.

Dilute the solution of chloride of iron with 4,500 C.c. of distilled water. Dissolve the ferrocyanide of potassium in 3,000 C.c. of distilled water. Filter both liquids. Add the solution of ferrocyanide of potassium,

slowly and with constant stirring, to the solution of chloride of iron. Let the precipitate settle, and wash it first by decantation, changing the wash water as frequently as practicable; then transfer the magma to a wetted muslin strainer and continue the washing until the washings are tasteless. Let drain, and dry it on the muslin, spread in a thin layer. If necessary, finish the drying on glass plates in the drying chamber. Reduce the product to a fine powder.

Reaction.— $8K_4FeCy_6 + 2Fe_2Cl_6 = 12KCl + Fe_4(FeCy_6)_2$.

Notes.—The dilute condition of the solutions is necessary because the precipitate is very voluminous. It is also necessary that the ferric chloride should be in excess over the potassium ferrocyanide throughout the reaction, that for this purpose the cyanide should be added to the chloride and not *vice versa*, and that some ferric chloride should remain undecomposed at the end. Otherwise the product will be contaminated with more potassium salt than when the directions given are observed. Under any circumstances there will be a slight amount of potassium compound in the product. Any attempt to wash out all the potassium salt will result in the formation of ferric oxide which remains in the preparation.

The precipitate is a voluminous magma which is difficult to wash, as it settles very slowly. Washing on a filter is impracticable, because the precipitate completely closes the pores of the paper.

The presence of a little free HCl in the liquid (which will be insured by using the solution of ferric chloride of the U. S. P.) considerably facilitates the washing.

Description.—A dark blue powder or solid mass commonly known as Prussian blue. It is insoluble in water and very dilute acids. It forms a soluble compound with strong solution of oxalic acid, which was formerly much used as an ink.

Tests.—It is decomposed by strong mineral acids with liberation of prussic acid. Strongly heated in the air it burns like tinder, leaving ferric oxide.

The powder loses about 25 per cent. of water by application of moderate heat.

Soluble Prussian blue is obtained when a solution of ferric chloride is added to a solution of potassium ferrocyanide, leaving the latter in excess. A precipitate is first formed, but when the mother liquor is washed away the precipitate is found to be soluble in pure water.

MERCURIC CYANIDE.

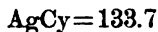
HYDRARGYRI CYANIDUM.

$HgCy_2 = 252$.

Prepared by dissolving mercuric oxide in hydrocyanic acid. This is effected by conducting hydrocyanic acid gas into a receiver containing water and mercuric oxide. The solution obtained is treated with mercuric oxide until all odor of hydrocyanic acid has ceased, and then evaporated to crystallization.

Description.—A white crystalline solid soluble in water and commercial alcohol, but almost insoluble in absolute alcohol. Its solution in water dissolves mercuric oxide, leaving on evaporation mercuric oxycyanide. Mercuric cyanide is decomposed by dilute hydrochloric acid with liberation of prussic acid.

Tests.—The aqueous solution should not be alkaline to test paper. A 5 per cent. solution acidified with dilute nitric acid should not become turbid on addition of silver nitrate solution (absence of chlorides).

SILVER CYANIDE.**ARGENTI CYANIDUM.**

Prepared by passing hydrocyanic acid gas into a solution of silver nitrate.

Reaction.— $\text{AgNO}_3 + \text{HCy} = \text{AgCy} + \text{HNO}_3$.

Description.—A white precipitate insoluble in water and dilute nitric acid, but soluble in ammonia water and solutions of alkali cyanides.

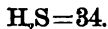
Tests.—Strongly heated, it should give off cyanogen, leaving metallic silver.

CHAPTER XV.**SULPHIDES.**

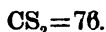
The sulphides of potassium and calcium are used in medicine in an impure state; both are water-soluble. The sulphides of mercury and antimony are insoluble.

HYDROSULPHURIC ACID.**ACIDUM HYDROSULPHURICUM.**

[HYDROGEN SULPHIDE.]



The process of preparing this gas as a reagent has been given in a former chapter

CARBON BISULPHIDE.**CARBONEI BISULPHIDUM.**

Carbon bisulphide is frequently employed as a solvent in analytical chemistry.

The pure liquid does not possess the disagreeable odor of the common commercial preparation.

SULPHURATED POTASSA.**POTASSA SULPHURATA.**

[LIVER OF SULPHUR.]

Sublimed sulphur..... 1 part.

Carbonate of potassium..... 2 parts.

Rub the carbonate of potassium previously dried, with the sulphur, and heat the mixture gradually, in a covered crucible, until it ceases to swell and is completely melted. Then pour the liquid on a marble slab, and, when it has solidified and become cold, break it into pieces, and keep it in a well stoppered bottle of hard glass.

Reaction.—With the proportions given in this formula, and if the temperature is not too high, the product is formed as follows: $4\text{K}_2\text{CO}_3 + 5\text{S}_8 = 3\text{K}_2\text{S}_8 + \text{K}_2\text{SO}_4 + 4\text{CO}_2$.

Notes.—The potassium carbonate must be finely powdered and intimately mixed with the sulphur in order to obtain a uniform product. It is best to sift the mixed powders through a No. 60 or No. 80 sieve.

A covered iron dish will answer well for the operation, and moderate heat (150° — 250° C.) will suffice. The mass should be occasionally stirred. When the evolution of carbon dioxide ceases, and the mass fuses quietly and completely, a sample should be taken out and put into twice its weight of water; when it dissolves entirely, without separation of sulphur, the fused mass is allowed to cool somewhat, and is then poured out into an oiled iron dish, or on a slab, and covered well (with a bell-glass or otherwise) to exclude air until it is cold. It is then broken into pieces and put away in a dry bottle, which must be tightly closed.

Description.—Irregular pieces of a liver-brown color when freshly prepared, turning gradually to greenish yellow or brownish yellow, having a faint, disagreeable odor, a bitter, alkaline, repulsive taste, and an alkaline reaction. Soluble in about 2 parts of water at 15° C. (59° F.), with the exception of a small residue; partly soluble in alcohol, the latter leaving undissolved the accompanying impurities. The aqueous solution has an orange yellow color and exhales the odor of hydrogen sulphide. The latter is abundantly evolved on the addition of hydrochloric acid, while, at the same time, sulphur is deposited. If a solution of the salt be boiled with an excess of hydrochloric acid, until no more hydrogen sulphide is given off, the cold filtrate, after being neutralized with soda, yields a white, crystalline precipitate with a saturated solution of bitartrate of sodium.

Tests.—On triturating together 10 parts of sulphurated potassa and 12.69 parts of crystallized sulphate of copper with 60 parts of water, and filtering, the filtrate should remain unaffected by hydrogen sulphide (presence of at least 56 per cent. of true sulphide of potassium).

SODIUM SULPHIDE.

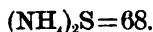
SODII SULPHIDUM.



A crystalline solid, very soluble in water, sometimes used as a reagent in analytical chemistry.

AMMONIUM SULPHIDE.

AMMONII SULPHIDUM.



This solution is a liquid reagent of great importance in analysis. Its preparation will be explained in the proper place.

AMMONIUM SULPHYDRATE.



A liquid reagent similar to the foregoing.

SULPHURATED LIME.

CALX SULPHURATA.

A mixture consisting chiefly of sulphide and sulphate of calcium ($3\text{CaS} \cdot \text{CaSO}_4$, 352).

Lime, in very fine powder 10 parts.

Precipitated sulphur 9 parts.

Mix the lime and sulphur intimately, and, having packed the mixture with gentle pressure into a crucible so as to nearly fill it, and having luted down the cover, expose the crucible for one hour to a low red heat, by means of a charcoal fire so arranged that the upper part of the crucible shall be heated first. Then remove the crucible, allow it to cool, rub its contents to powder, and at once transfer them to small, glass stoppered vials.

Notes.—The reactions occurring are analogous to those which take place when sulphurated potassa is made. The most important constituent of the product is the calcium sulphide, or perhaps a mixture of several calcium sulphides is present. Calcium thiosulphate is probably also contained in the preparation.

The Pharmacopœia says that "this preparation is to be dispensed when sulphide of calcium is prescribed."

In the new British Pharmacopœia the process for preparing "sulphurated lime" is as follows :

Calcium sulphate, in fine powder 7 parts.

Wood charcoal, in fine powder 1 part.

Mix thoroughly. Heat to redness in an earthen crucible until the black color has disappeared. Cool, and at once put the residue in a stoppered bottle.

It should contain not less than 50 per cent. of calcium sulphide (CaS).

Reaction.— $\text{CaSO}_4 + 2\text{C} = \text{CaS} + 2\text{CO}_2$.

SOLUTION OF SULPHURATED LIME.

LIQUOR CALCIS SULPHURATÆ.

Sublimed sulphur 250 Gm.

Calcium hydrate 100 Gm.

Water 1,000 C.c.

Boil together for one hour. Let settle, and decant.

Contains calcium sulphide and calcium hyposulphite.

(See title, Precipitated Sulphur.)

It is a dark red brown liquid, having a strong odor of hydrogen sulphide.

FERROUS SULPHIDE.

FERRI SULPHIDUM.

$\text{FeS} = 88$.

This is a heavy black solid, prepared by fusing scrap iron with sulphur.

It is used for the preparation of hydrogen sulphide by the action of hydrochloric acid.

BLACK MERCURY SULPHIDE.

HYDRARGYRI SULPHIDUM NIGRUM.

Mercury 1 part.

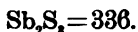
Sublimed sulphur 1 part.

Triturate together until all globules of mercury have disappeared, and a uniform black powder is obtained.

The product is a mixture of mercuric sulphide and sulphur.

PURIFIED SULPHIDE OF ANTIMONY.

ANTIMONII SULPHIDUM PURIFICATUM.



Sulphide of antimony	2 parts.
Water of ammonia	1 part.

Reduce the sulphide of antimony to a very fine powder. Separate the coarser particles by elutriation, and, when the finely divided sulphide has been deposited, pour off the water, add the water of ammonia, and macerate for five days, agitating the mixture frequently. Then let the powder settle, pour off the water of ammonia, and wash the residue by repeated affusion and decantation of water. Finally, dry the product by the aid of heat.

Note.—By this treatment all but traces of arsenic is removed.

Description.—A heavy dark gray powder, insoluble in water and alcohol, but soluble with decomposition in boiling strong hydrochloric acid. The solution so obtained is precipitated by addition of water.

Tests.—Fuses with a mixture of sodium nitrate and carbonate to a white mass, which can be examined according to the process given for the separation of the third group of elements under the head of Qualitative Analysis.

SULPHURATED ANTIMONY.

ANTIMONIUM SULPHURATUM.

Chiefly antimonious sulphide (Sb_2S_3 , 336) with a very small amount of antimonious oxide.

Purified sulphide of antimony	1 part.
Solution of soda	12 parts.
Diluted sulphuric acid, sufficient.	

Mix the sulphide of antimony with the solution of soda and 30 parts of distilled water, and boil the mixture over a gentle fire for two hours, constantly stirring, and occasionally adding distilled water so as to preserve the same volume. Strain the liquid immediately through a double muslin strainer, and drop into it, while yet hot, diluted sulphu-

ric acid so long as it produces a precipitate. Wash the precipitate with hot distilled water until the washings are at most but very slightly clouded by test solution of chloride of barium; then dry the precipitate and rub it to a fine powder,

Reaction.—First, $\text{Sb}_2\text{S}_3 + 6\text{NaOH} = \text{Na}_3\text{SbO}_3 + \text{Na}_2\text{SbS}_3 + 3\text{H}_2\text{O}$; then $2\text{Na}_3\text{SbO}_3 + 3\text{H}_2\text{SO}_4 = 3\text{Na}_2\text{SO}_4 + \text{Sb}_2\text{O}_3 + 3\text{H}_2\text{O}$, and $2\text{Na}_2\text{SbS}_3 + 3\text{H}_2\text{SO}_4 = 3\text{Na}_2\text{SO}_4 + \text{Sb}_2\text{S}_3 + 3\text{H}_2\text{S}$.

Description.—A reddish brown powder, insoluble in water or alcohol, dissolves when heated with strong hydrochloric acid in considerable excess, but with decomposition. Hydrogen sulphide is given off, and the solution contains antimony chloride, which is precipitated by water.

Tests.—The powder should give nothing to boiling water.

Dissolve a Gm. or two of it, as described under the foregoing, and test for other metals.

ANTIMONIC SULPHIDE.

ANTIMONII SULPHIDUM FLAVUM.

$\text{Sb}_2\text{S}_3 = 400$.

Purified black sulphide of antimony	18 parts.
Sublimed sulphur	4 parts.
Soda	13 parts.
Water	50 parts.
Sulphuric acid, distilled water, each sufficient.	

Triturate the antimonious sulphide and the sulphur together until mixed; add the mixture to the soda previously dissolved in the water; boil the mixture with constant stirring about fifteen minutes, or until no more of the powder dissolves. Filter, evaporate the filtrate, and let it cool, that crystals may form. Rinse the crystals hastily with a little weak soda solution, and dry them by pressing them between bibulous paper. (These crystals are the so-called "Schlippe's Salt"— $\text{Na}_3\text{SbS}_4 + 9\text{H}_2\text{O}$). Dissolve 100 parts of these crystals in 400 parts of distilled water. Filter, if necessary. Dilute the filtrate with six hundred parts of distilled water, and pour the dilute solution slowly and with constant stirring into a mixture of thirty-six parts (by weight) of sulphuric acid and six hundred parts of distilled water. Wash the precipitate as rapidly as possible, by affusion and decantation, with distilled water, let drain, express the remainder of the water, and dry the precipitate with the aid of gentle heat. Keep it in a tightly corked bottle.

Reaction.— $4\text{Sb}_2\text{S}_3 + 4\text{S} + 18\text{NaOH} = 5\text{Na}_3\text{SbS}_4 + 3\text{NaSbO}_3 + 9\text{H}_2\text{O}$;
then, $2\text{Na}_3\text{SbS}_4 + 3\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O} = \text{Sb}_2\text{S}_3 + 3\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + 3\text{H}_2\text{S}$.

Notes.—The direction to wash the crystals of Schlippe's salt is given for the purpose of removing sulpharsenate, which is more readily soluble, and a little soda is added to the wash-water in order to prevent oxidation.

The sulphuric acid must be in excess; otherwise the product will be dark colored.

The washing must be done with distilled water, and should not be long continued. Affusion and decantation is therefore to be preferred.

Must be protected against exposure to light.

Description.—An orange yellow powder, insoluble in water or alcohol. It is decomposed by heat, sulphur being evolved, and the black sulphide left.

Tests.—It should give nothing to water.

It should yield a perfectly white mass when fused with an excess of sodium nitrate and carbonate. The fused mass can be used for the tests for arsenic, as described later in detail.

OXYSULPHURET OF ANTIMONY.

ANTIMONII OXYSULPHURETUM.

[KERMES MINERAL.]

Purified antimony sulphide.....	1 part.
Sodium carbonate.....	25 parts.

Put the sodium carbonate, together with 250 parts of water, into an iron pot, and heat to boiling. Add the sulphide and continue boiling for two hours, stirring constantly, and replacing the water lost by evaporation. Filter, as rapidly as possible, and while still hot, into a warm porcelain dish or stone jar kept in hot water, so that the filtrate will cool very slowly. When cold, decant the clear liquid from the precipitate, collect the latter at once on a filter, and wash it with cold distilled water until the washings no longer give an alkaline reaction on test-paper, or until the washings begin to be colored. Then press the precipitate between blotting paper, and afterwards dry it in a dark place at a temperature not exceeding 30° C. (86° F.). When dry, powder it, and keep it in tightly closed bottles, protected from light.

Reaction.— $3\text{Na}_2\text{CO}_3 + \text{Sb}_2\text{S}_3 = 3\text{Na}_2\text{S} + \text{Sb}_2\text{O}_3 + 3\text{CO}_2$; and $3\text{Na}_2\text{S} + \text{Sb}_2\text{O}_3 + \text{Na}_2\text{CO}_3 = 2\text{NaSbO}_3 + 6\text{NaSbS}_2 + \text{CO}_2$; or, stated in one equation, $4\text{Na}_2\text{CO}_3 + 4\text{Sb}_2\text{S}_3 = 2\text{NaSbO}_3 + 6\text{NaSbS}_2 + 4\text{CO}_2$.

Notes.—The hot solution of sodium sulphantimonite holds in solution a considerable quantity of antimonious sulphide, which, on cooling, deposits together with antimonious oxide. The quantity of soda used is over twenty times the quantity theoretically required by the equation; but this is done to prevent the antimony oxide, as far as possible, from depositing. The boiling should not be continued longer than the prescribed time, and the washing should be concluded without delay, to prevent oxidation.

By boiling the residue with the liquid a second time, another crop is obtainable, but this is richer in oxide and hence not of proper composition. Caustic alkalis can be used instead of carbonate, but the product then obtained does not have the same handsome appearance. A large quantity of water is employed in order that the antimonious oxide may not crystallize out. For the same reason the liquid is not to be allowed to cool rapidly, but the temperature is made to fall very gradually from the boiling heat down to about 40° C. (104° F.) during a period of several hours. The dilute character of the liquid facilitates the depo-

sition of the kermes, which is readily completed at the temperature named. A more concentrated solution of sulphantimonite of sodium would have a greater solvent power on the kermes, which would then be held in solution until the liquid is cooled to a much lower temperature, and the product would then at the same time contain an undue proportion of oxide.

Description.—Properly prepared, kermes is a beautiful, velvety, dark purplish brown powder, containing antimonious sulphide and antimonious oxide in varying proportions. Little crystals of the oxide are seen under the microscope as shining particles.

Tests.—Examine for foreign metals, as already indicated for other antimony sulphides.

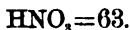
CHAPTER XVI.

NITRATES.

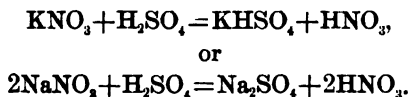
Basic nitrates of mercury and bismuth are insoluble in water; normal nitrates of these metals are split up by water into basic and acid salts. All the other nitrates are water soluble. The nitrates may generally be prepared by saturating nitric acid with the metals or their oxides, hydrates, or carbonates.

NITRIC ACID.

ACIDUM NITRICUM.



To obtain hydrogen nitrate, potassium or sodium nitrate is decomposed by hydrogen sulphate:



Theoretically, 101 parts of potassium nitrate yield 63 parts of HNO_3 , corresponding to about 90 parts of the official nitric acid (69.4 per cent. HNO_3). The potassium-hydrogen sulphate does not decompose potassium nitrate until the temperature is so high as to decompose the nitric acid; hence it requires twice as much sulphuric acid to make nitric acid from potassium nitrate as it does to make the same quantity of nitric acid from sodium nitrate, which is decomposed by sodium-hydrogen sulphate. The proportions to be used are, therefore, 1010 parts of potassium nitrate and 980 parts of H_2SO_4 (corresponding to 1020 parts of official sulphuric acid); or 850 parts of sodium nitrate and 510 parts of concentrated sulphuric acid. If sodium nitrate is used, the sulphuric acid must be diluted with one-fourth its weight of water to prevent foaming. This foaming is caused by the abstraction of water from the nitric acid by the sodium-hydrogen sulphate, which results in the decomposition of the acid.

By using enough sulphuric acid to obtain a residue of acid sulphate, the reaction can be effected at a lower temperature than if the minimum quantity be employed, and there is then less decomposition of the nitric acid. The usual practice is to employ about 150 parts of concentrated sulphuric acid, diluted with 38 parts of water, to 170 parts of sodium nitrate.

An experiment illustrating this manufacture has been given in Part I.

Impurities.—The most common impurities in commercial nitric acid are H_2SO_4 , Cl , NO_2 , and iron nitrate. The chlorine is derived from the chlorides in the nitrates employed. Chili saltpeter also contains sodium iodide, which gives rise to contamination with iodine chloride. The iron comes from the iron cylinders in which the distillation is conducted in the manufacture of nitric acid on a large scale. [Absolute nitric acid (1.52 sp. gr.) does not attack metallic iron, and the strong acid generated in the iron cylinders attacks the metal but little. Hence iron cylinders can be used.] The yellow or reddish color of crude strong nitric acid is due mostly to nitrogen peroxide (nitrogen tetroxide, N_2O_4 , or hyponitric acid). This impurity may be removed by heating the acid to about 80° to 90° C., whereby NO_2 is driven off.

Purification.—This is effected on a large scale by re-distillation from glass retorts. The first portion distilling over contains the nitric peroxide, chlorine and iodine. As soon as the distillate is colorless and free from chlorine, the receiver is changed, and the distillation continued until about one-eighth remains. To fix the sulphuric acid in the crude nitric acid, a little potassium nitrate is added before the distillation.

The chlorine as well as the nitrogen peroxide may be driven off by carefully heating the crude nitric acid in a dish or flask about one or two hours before the distillation is undertaken. The loss of nitric acid by this evaporation is trifling. In order to eliminate the chlorine perfectly, the nitric acid must have at least 1.34 specific gravity.

Pure nitric acid is made directly from pure potassium nitrate and pure sulphuric acid.

Properties.—An extremely acid, corrosive, fuming liquid, of a peculiar, stifling odor. It contains 69.4 per cent. of absolute nitric acid (HNO_3) and 30.6 per cent. of water. The specific gravity is 1.42, corresponding to 48° Beaumé. Nitric acid applied to organic substances causes a yellow discoloration, especially of nitrogenous matters, as woolen fabrics and other animal products.

Relation of weight to volume.—The specific gravity of the official acid being 1.42, its specific volume is 0.704. The usual half-gallon acid bottle holds about 7 avoirdupois pounds of this acid.

Action on metals.—Gold, platinum, iridium, rhodium, and chromium are not affected by nitric acid. Iron, lead and silver are scarcely attacked by concentrated nitric acid, but diluted nitric acid dissolves them. Antimony, tin and tungsten are oxidized but not dissolved. Mercury, silver and bismuth dissolve readily, especially in warm nitric acid, with the evolution of nitric oxide (N_2O), which, in contact with the air, at once oxidizes to nitrogen tetroxide (N_2O_4), which appears as red fumes.

Tests.—The Pharmacopoeial tests apply only to an acid at least equal in purity to that sold by chemical manufacturers under the designation of "chemically pure" ("C. P.").

It must be colorless. Volatilizes without residue. The actual strength of the acid can be ascertained by accurately diluting 50 C.c. with distilled water so as to make 500 C.c., and then testing this by means of the standard volumetric solution of sodium hydrate, as described later.

Preservation.—Must be kept in glass stoppered bottles, in a cool place, and protected from light.

Uses.—Pharmaceutically, nitric acid is used as an oxidizing agent; for the preparation of other nitrates; nitro-hydrochloric acid, etc.

Saturating power.—100 parts of the official (U. S.) nitric acid, containing 69.4 per cent. of HNO_3 , will saturate:

Potassa (100 per cent. KOH), 61.69 parts	}	Yielding 111.26 parts of potassium nitrate.
Potassa (90 per cent.), 68.54 parts		
Solution of potassa (5 per cent.), 1288.8 parts ..		
Potassium carbonate (81 per cent.), 98.83 parts ..		
Potassium bicarbonate, 110.16 parts		
Soda (100 per cent. NaOH), 44.06 parts	}	Yielding 98.63 parts of sodium nitrate.
Soda (90 per cent.), 48.95 parts		
Solution of soda (5 per cent.), 881.20		
Sodium carbonate (96 per cent.), 164.09 parts ..		
Sodium bicarbonate (99 per cent.), 98.47 parts ..		
Ammonia (NH_3), 18.72 parts	}	Yielding 88.18 parts of ammonium nitrate.
Ammonia water (10 per cent.), 187.20 parts ..		
Ammonia water, stronger (28 per cent.), 66.87 parts		
Ammonium carbonate, 57.66 parts.		

Specific Gravity and Percentage Strength of Solutions of HNO_3 .

(Kolb.)

Per cent. of HNO_3	Sp. gr. 60°	Sp. gr. 15°
5	1.031	1.029
10	1.070	1.060
15	1.099	1.089
20	1.132	1.120
30	1.200	1.185
40	1.267	1.251
50	1.334	1.317
60	1.393	1.374
70	1.444	1.423
80	1.484	1.460
90	1.522	1.495
100	1.559	1.530

Strength.—The U. S. Pharmacopœia prescribes an acid of 69.4 per cent. HNO_3 , having 1.42 sp. gr. Other Pharmacopœias apply the same title to acids of various strengths.

Pharmacopœia.	Per cent. HNO_3 .	Specific gravity.	Number of parts representing 68 parts of HNO_3 .
U. S. (1892).....	69.4	1.42	90.78
Gt. Britain (1885).....	69.4	1.42	90.78
France (1884).....	68.6	1.39	99
Netherlands (1871).....	53-54	1.33-1.34	116
Spain (1865).....	51	1.32	123.4
Austria (1869).....	48	1.30	131.25
Russia (1880).....	32.67	1.20	192.8
Germany (1882).....	80	1.185	210
Sweden (Norway & Denmark) '69	29.17	1.18	216
Switzerland (1872).....	21.67	1.13	290.8

DILUTED NITRIC ACID.

ACIDUM NITRICUM DILUTUM.

Nitric acid..... 1 part.

Distilled water..... 6 parts.

Mix. Keep the product in glass stoppered bottles.

Description.—A colorless liquid, which should leave no residue on evaporation. It has the sp. gr. 1.059, and the sp. vol. 0.944.

Tests.—Determine strength by means of sodium hydrate solution after dilution with known amount of water.

Saturating power.—100 parts of the official (U. S.) diluted nitric acid, containing 10 per cent. of HNO_3 , will saturate :

Potassa (90 per cent.), 9.88 parts.....	}	Yielding 16.03 parts of potassium nitrate.
Solution of potassa (5 per cent.), 177.78 parts.....		
Potassium carbonate (81 per cent.), 13.52 parts.....		
Potassium bicarbonate, 15.87 parts.....	}	Yielding 13.49 parts of sodium nitrate.
Soda (90 per cent.), 7.05 parts.....		
Solution of soda (5 per cent.), 126.98 parts.....		
Sodium carbonate (96 per cent.), 23.64 parts.....	}	Yielding 12.70 parts of ammonium nitrate.
Sodium bicarbonate (99 per cent.), 13.47 parts.....		
Ammonia water (10 per cent.), 26.98 parts.....		
Ammonia water, stronger (28 per cent.), 9.64 parts.....	}	
Ammonium carbonate, 8.81 parts.....		

POTASSIUM NITRATE.

POTASSII NITRAS.

$\text{KNO}_3 = 101$.

Prepared from crude sodium nitrate by double decomposition with potassium chloride. The method is based upon the differences in solubility of the salts at different temperatures. Potassium nitrate is not as readily soluble in cold water as the chlorides of potassium and sodium

are; but in hot water the chlorides are much less soluble than the potassium nitrate. Thus 100 parts of water at 0° C. (32° F.) will dissolve only 13.3 parts of potassium nitrate, but 29.3 parts of potassium chloride and 35.5 parts of sodium chloride; at 100° C. (212° F.), however, 100 parts of water will dissolve 240 to 250 parts of potassium nitrate, but only 57 parts of potassium chloride and 39.9 parts of sodium chloride. When sodium nitrate and potassium chloride are mixed in water no reaction takes place until the liquid is boiled down; but when the double decomposition takes place the sodium chloride precipitates already at a high temperature, and is separated from time to time. To facilitate the reaction the sodium nitrate is kept in excess over the potassium chloride.

The product which crystallizes out is sufficiently pure to be fit for most uses without re-crystallization. It contains less than 1 per cent. of sodium chloride.

Purification.—Commercial potassium nitrate may be purified by dissolving it in an equal weight of boiling, distilled water, filtering, and stirring the filtrate constantly until cool. The saltpeter should first be coarsely powdered to facilitate its solution.

When cool, set it aside for some hours. Collect the crystals on a filter, and let drain. Wash twice by rapidly passing small quantities of distilled water over the crystals, allowing all of the wash-water to pass through before adding more. When the washings no longer give a decided reaction for chlorides (with test solution of silver nitrate), collect the crystals and dry them between blotting paper, or on suitable trays covered with muslin.

Evaporate the mother liquor at about 95° C. (203° F.) to one-third its bulk, and let cool during constant stirring. Wash the second crop of crystals as before, drain, and dry as before, and add them to the first crop. Repeat this operation as often as may be profitable.

To simply granulate potassium nitrate it may be dissolved in an equal weight of boiling distilled water, the solution filtered, and the filtrate evaporated, stirring constantly with a glass rod or porcelain spatula until a dry, granular salt remains.

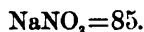
Description.—Colorless, anhydrous crystals, very soluble in hot water, readily soluble in cold, and nearly insoluble in alcohol. They fuse without decomposition, unless the heat be too high. In this case oxygen is given off and nitrite and oxide of potassium left.

The salt is permanent in dry air, neutral and without odor.

Tests.—It should give a perfectly clear solution with water. This acidulated with nitric acid should not become more than opalescent when treated with solution of silver nitrate for chlorides, or of barium chloride for sulphates. On mixing 2.02 Gm. of the dry powdered salt with the same weight of strong sulphuric acid, evaporating to dryness and igniting, a residue of sulphate, weighing 1.74 Gm., should be obtained.

SODIUM NITRATE.

SODII NITRAS.



Crude sodium nitrate occurs native in Peru and Bolivia. The native sodium saltpeter contains from 20 to 80 per cent. of sodium nitrate,

most frequently yielding 50 per cent. It is freed from earth and other impurities by solution, straining, and crystallization.

It is purified in the same way as potassium nitrate, by re-crystallization and by washing with a cold saturated solution of pure sodium nitrate, which removes chlorides present.

Description.—Colorless crystals, slightly deliquescent, very soluble in water, and but slightly soluble in alcohol.

Fuses at a moderate heat, and at a higher temperature decomposes, leaving some sodium nitrite.

Tests.—It should give a clear solution with water. This solution should not give a reaction for more than slight traces of chlorides and sulphates when treated with the proper reagents.

AMMONIUM NITRATE.

AMMONII NITRAS.



Prepared by neutralizing dilute nitric acid with ammonia or ammonium carbonate, filtering, and evaporating the solution to crystallization. The crystals are kept in a state of fusion at not above 160° C. (320° F.) until the salt ceases to give off watery vapors.

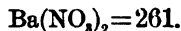
Description.—Colorless, slightly deliquescent prismatic crystals, very soluble in water and readily soluble in alcohol.

By application of strong heat they break up into water and nitrogen monoxide.

Tests.—Complete solubility in water, yielding a clear liquid. Volatility without residue. Absence of sulphates and chlorides when tested with solutions of barium nitrate and silver nitrate.

BARIUM NITRATE.

BARII NITRAS.



Prepared by neutralizing nitric acid with barium carbonate, and evaporating to crystallization.

Description.—Colorless crystals, soluble in about 11 parts of water at 20°, very slightly soluble in alcohol.

Tests.—The solution should be completely precipitated by diluted sulphuric acid. The aqueous solution should give no test for chlorides with nitrate of silver.

SOLUTION OF ALUMINIUM NITRATE.**LIQUOR ALUMINII NITRATIS.**

Containing about 10 per cent. of $\text{Al}_2(\text{NO}_3)_6 \cdot 18\text{H}_2\text{O} = 750$.

Alum, powdered.....	33 parts.
Sodium carbonate	30 parts.
Nitric acid.....	20 parts.

Dissolve the alum and the sodium carbonate separately, each in 450 parts of boiling water; filter the solutions; pour the solution of alum into the solution of sodium carbonate, stirring briskly. Add 300 parts of boiling water. Digest the mixture at a gentle heat until the evolution of carbon dioxide ceases; wash the precipitate with hot distilled water, first by decantation and afterward on a muslin strainer, until the washings cease to give a precipitate with test-solution of barium chloride. Let the magma drain thoroughly, and then dissolve it in the nitric acid. Evaporate the solution to 260 parts.

Notes.—The reaction taking place between the alum and sodium carbonate, and notes on that part of the process, are given under the title, Aluminium Hydrate.

NITRATES OF IRON.**FERROUS AND FERRIC NITRATES.**

Metallic iron is readily dissolved in nitric acid. If the acid is largely diluted and cold the metal is dissolved without any evolution of gas, and the solution will contain ferrous nitrate and ammonium nitrate. But if the acid is more concentrated, red vapors are given off, and ferric nitrate is formed.

The "Solution of Pernitrate of Iron" of the British Pharmacopœia is directed to be made as follows:

Iron wire, cut.....	10 Gm.
Nitric acid.....	45 C.c.

Dilute the acid with 160 C.c. of distilled water, add the iron, and let the metal dissolve, taking care to control the reaction, in case it should be too violent, by adding a little cold distilled water. When all the iron is dissolved, filter the solution and add to it enough distilled water to make the final product 300 C.c.

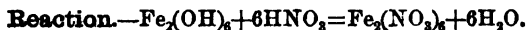
This solution has 1.107 sp. gr., and is stronger than that of the United States Pharmacopœia, which is prepared as follows:

SOLUTION OF FERRIC NITRATE.**LIQUOR FERRI NITRATIS.**

An aqueous solution containing 6 per cent. of anhydrous ferric nitrate ($\text{Fe}_2(\text{NO}_3)_6$, 484).

Solution of normal ferric sulphate.....	18 parts.
Water of ammonia.....	15 parts.
Nitric acid.....	7 parts.

Dilute the solution of ferric sulphate with 100 parts of cold water. Pour it gradually into the ammonia water previously diluted with 40 parts of water. Wash the ferric hydrate in the usual way (see under title, Ferric Hydrate) until the washings are only slightly clouded by test solution of barium chloride. Drain well, and transfer the magma to a porcelain capsule; add the nitric acid and stir well until solution results. Finally, add enough water to make the whole weigh 100 parts.

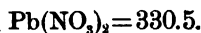


Notes.—This formula yields a very satisfactory product if properly carried out. Formerly the preparation was made by dissolving iron in nitric acid; the product then varied according to the degree of concentration of the acid and the temperature employed.

Description.—A reddish colored solution with acid reaction, and strong styptic taste.

The specific gravity of the solution is 1.05, and its sp. vol. 0.952.

Tests.—Should be completely precipitated by ammonium hydrate. Barium nitrate and silver nitrate should not produce precipitates indicating sulphates or chlorides.

LEAD NITRATE.**PLUMBI NITRAS.**

Lead oxide, in fine powder.....	18 parts.
Nitric acid.....	15 parts.
Water.....	75 parts.

Heat the ingredients together in a capsule on a water-bath until the lead oxide is dissolved; filter the solution, evaporate it to 50 parts, and then set aside to crystallize. Evaporate the mother liquor to obtain a second crop of crystals.



Description.—Heavy white crystals. Readily soluble in water, and but very slightly in alcohol. Strongly heated, they decompose, yielding lead monoxide, oxygen, and nitrogen tetroxide.

Tests.—Complete solubility in water. The solution should be completely precipitated by addition of dilute sulphuric acid or hydrogen sulphide.

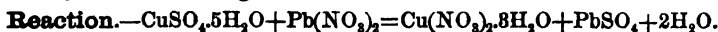
COPPER NITRATE.

CUPRI NITRAS.



Copper sulphate	50 parts.
Lead nitrate	33 parts.

Dissolve the salts, each separately, in 200 parts of water, filter the solutions and mix them. Reject the precipitated lead sulphate, filter the liquor which contains the cupric nitrate, and evaporate it until it yields crystals on cooling.



Notes.—Copper dissolves readily in dilute nitric acid, $3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}.$ Copper nitrate can therefore be made by that method. On evaporation of the solution the salt is obtained in handsome blue crystals.

MERCUROUS NITRATE.

HYDRARGYRI PROTONITRAS.



Mercury dissolves in nitric acid with greater or less rapidity according to the temperature and the degree of concentration of the acid. When strong nitric acid is used the solution will contain mercuric nitrate, which, however, is reduced to mercurous nitrate by digestion with more mercury. By dissolving mercury in cold dilute nitric acid, mercurous nitrate is obtained. The acid should be present in excess, because otherwise basic salts are formed which are insoluble in the liquid. The salt may be obtained from the solution in colorless plates which can be dissolved in a small quantity of water, but which decompose if much water is added, an acid mercurous nitrate remaining in solution whilst a yellow basic mercurous nitrate precipitates. A dilute solution of mercurous nitrate can therefore not be made without an excess of nitric acid. On heating the neutral mercurous nitrate with more mercury, various basic salts may be formed, according to the quantity of mercury dissolved, and all of these mercurous nitrates are decomposed by water.

SOLUTION OF MERCURIC NITRATE.**LIQUOR HYDRARGYRI NITRATIS.**

An aqueous solution containing about 50 per cent. of mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$, 324) with free nitric acid.

Red mercuric oxide	8 parts.
Nitric acid	9 parts.
Distilled water	3 parts.

Mix the acid and water and dissolve the oxide in the mixture.

Keep the solution in glass stoppered bottles.

Reaction.— $\text{HgO} + 2\text{HNO}_3 = \text{Hg}(\text{NO}_3)_2 + \text{H}_2\text{O}$.

Description.—A colorless, or nearly colorless, heavy liquid, with strong acid reaction.

Its specific gravity is 2.10, and its sp. vol. 0.476.

Tests.—The addition of distilled water should not render the solution turbid from precipitation of basic mercurous salt.

The addition of dilute hydrochloric acid should not produce a white precipitate of mercurous chloride.

The "Liquor Hydrargyri Nitratis Acidus" of the British Pharmacopœia is prepared as follows:

Mercury	400 Gm.
Nitric acid	500 C.c.
Distilled water	150 C.c.

Mix the acid and water in a flask. Dissolve the mercury in the mixture without the aid of heat. Then boil gently for fifteen minutes, or until a drop of the liquid no longer gives any precipitate in dilute hydrochloric acid. Let it cool, and preserve the solution, which should weigh about 1,200 Gm., in a stoppered bottle away from the light.

Reaction.— $3\text{Hg}_2 + 16\text{HNO}_3 = 6\text{Hg}(\text{NO}_3)_2 + 2\text{N}_2\text{O}_4 + 8\text{H}_2\text{O}$.

OINTMENT OF NITRATE OF MERCURY.**UNGUENTUM HYDRARGYRI NITRATIS.**

Mercury	7 parts.
Nitric acid	17 parts.
Lard oil	76 parts.

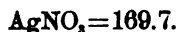
Heat the lard oil, in a porcelain capsule, to 70° C. (158° F.); then add, without stirring, 7 parts of nitric acid; continue the heat so long as a moderate effervescence continues, and allow the mixture to cool. Dissolve the mercury in the remainder of the nitric acid, with the aid

of sufficient heat to prevent the solution from crystallizing; add this solution to the mixture before it has become entirely cold, and mix thoroughly. Do not use an iron spatula.

Notes.—The reactions occurring when fat is treated with strong nitric acid are not well known; however, the lard oil is acted upon with more or less energy according to the temperature, and the olein is converted by oxidation at the expense of the nitric acid into elaidin, which is a firmer fat, having a fusing point of about 82° C. (89.6° F.). It is necessary that the nitric acid used should be of full strength in order that this reaction may be completed before the solution of mercuric nitrate is added. If the temperature is perfectly controlled, the acid used of full strength, and the reaction thoroughly completed before the nitrate of mercury is added, the product will be a handsome, firm, lemon yellow ointment. If the heat is too high, the mercury nitrate will be decomposed and the product rendered brown, or gray from mercury oxide and reduced metal. In mixing the mercuric nitrate solution with the oxidized fat, it is necessary to stir well with a porcelain spatula or glass rod until nearly cold, in order to thoroughly incorporate the heavy liquid which might otherwise settle to the bottom of the capsule.

SILVER NITRATE.

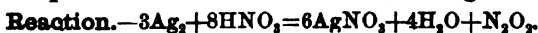
ARGENTI NITRAS.



Silver	30 parts.
Nitric acid	25 parts.
Distilled water	50 parts.

Add the nitric acid and the water to the metal in a flask, and heat gently until dissolved. Decant the clear liquid into a porcelain capsule, evaporate, and set aside to crystallize. Let the crystals drain in a glass funnel, and dry them by exposure to the air, carefully avoiding contact with organic matter.

Keep it in an amber colored bottle, with glass stopper.



Notes.—The metal dissolves rapidly at first, and with considerable evolution of heat. Afterwards, however, the reaction is slower as the solution becomes more concentrated. To prevent loss by spurting, the neck of the flask may be covered by a watch-crystal.

When large quantities are acted upon the flask may be set in a warm place and left for several days. The clear liquid is then decanted from the residue, and the latter is washed, the filtered washings being added to the other solution. It is best to have the metal present in excess so that a small quantity of it remains undissolved. By this precaution vapors of nitric acid are avoided in the subsequent evaporation. To remove copper, if present, the solution is evaporated to dryness and the mass fused in a thin porcelain capsule (Meissen dish) over a sand-bath, keeping the salt fused two or three hours until a small quantity of it, when removed from the dish, dissolved in water, and the solution filtered, is not turned blue by ammonia water. All of the copper nitrate which was present has now been reduced to cupric oxide. The mass is then poured into a clean polished iron dish or mortar, and allowed to cool; it cannot be allowed to cool in the porcelain dish for that will burst. The salt is then redissolved in distilled water, the solution is filtered, and crystallization effected. Both fused and crystallized silver nitrate are free from water.

When too strongly heated the fused nitrate is yellowish from nitrite. Exposure to light turns it gray from reduced metal when organic matter is present.

Description.—Colorless tabular crystals, very soluble in water, and slightly in alcohol.

The crystals have a metallic taste, and are very poisonous. Their specific gravity is 4.83. They fuse at a temperature of about 200° C., solidifying on cooling to a brittle crystalline mass, quite free from color.

Tests.—The crystals should be free from a yellow tinge, and should dissolve in water completely. Even when exposed to light the salt should remain uncolored.

.1697 Gm. of the crystals when dissolved in water should require 10 C.c. of $\frac{N}{10}$ sodium chloride solution for precipitation.

FUSED SILVER NITRATE.

ARGENTI NITRAS FUSUS.

Silver nitrate	100 parts.
Hydrochloric acid	4 parts.

Fuse the silver nitrate in a porcelain capsule on a sand-bath at as low a temperature as possible; then add the acid gradually, stirring well, and when nitrous vapors cease to be evolved, mould the salt into sticks or cones by means of a suitable mould of bright polished iron, or of silver.

Notes.—By the addition of hydrochloric acid, silver chloride is introduced into the preparation: $\text{AgNO}_3 + \text{HCl} = \text{AgCl} + \text{HNO}_3$. The object of this is to render the fused sticks more tough and strong.

Description.—A heavy opaque solid, usually of a grayish color.

About 95 per cent. of the mass is readily soluble in water. The remaining 5 per cent., consisting of chloride, is not. It is not so quickly soluble as the pure salt.

Tests.—When treated with water the chloride mentioned above fails to dissolve. When this is separated by filtration, dried and fused, it should form a compact hornlike mass, and amount to 5 per cent. by weight of the whole.

DILUTED SILVER NITRATE.

ARGENTI NITRAS DILUTUS.

Silver nitrate	1 part.
Potassium nitrate	1 part.

Fuse the salts together in a porcelain capsule over a sand-bath at as low a temperature as possible, stirring constantly until the mass flows quietly. Then cast the salt in moulds.

Less brittle than pure silver nitrate.

Description.—A hard solid, finely crystalline, and readily soluble in water. It has a metallic taste and caustic properties similar to the pure nitrate.

Tests.—Should dissolve in water without residue.

.3394 Gm. should require 10 C.c. of an $\frac{N}{10}$ sodium chloride solution for precipitation.

BISMUTH SUBNITRATE.**BISMUTHI SUBNITRAS.**

Bismuth, in small pieces	500 Gm.
Nitric acid	1,500 C.c.
Sodium carbonate	2,500 Gm.
Ammonia water	1,250 C.c.
Distilled water, sufficient.	

Mix 800 C. c. of the nitric acid with 1,000 C.c. of the distilled water in a capacious glass vessel, add the bismuth, and set aside for twenty-four hours to dissolve. Dilute the solution with 2,500 C.c. of distilled water, so that the turbidity produced by the addition of the water no longer disappears on stirring; stir well, and again set it aside for twenty-four hours. Then filter.

Dissolve the sodium carbonate in 5,000 C.c. of distilled water, with the aid of heat, filter the solution, and let it rest until cold. Then add the cold solution of bismuth nitrate very slowly, and with constant, active stirring, to the sodium carbonate solution. Transfer the whole to a wetted muslin strainer, let drain, wash with distilled water until the washings pass tasteless, and then let it drain again as completely as possible. Put the moist precipitate in a suitable vessel, gradually add the remainder of the nitric acid, being careful to avoid foaming over, and when all has dissolved, also add gradually 1,000 C.c. of distilled water, and set the solution aside for twenty-four hours. Then filter. Dilute the filtrate by adding gradually 6,000 C.c. of distilled water, stirring well. Then add to this, very slowly, the ammonia water, through a small siphon, stirring constantly. Transfer the whole at once to a strainer, and after draining rapidly, pour over the precipitate 8,000 C.c. of distilled water, let it drain again, and press out as much of the liquid as possible. Then dry the product on bibulous paper with a gentle heat, and rub it into powder.

Reaction.—First the bismuth is dissolved in the nitric acid to form normal bismuth nitrate, thus: $2\text{Bi} + 8\text{HNO}_3 = 2\text{Bi}(\text{NO}_3)_3 + 2\text{NO} + 4\text{H}_2\text{O}$. Then bismuth subcarbonate is made: $2\text{Bi}(\text{NO}_3)_3 + 8\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = (\text{BiO})_2\text{CO}_3 \cdot \text{H}_2\text{O} + 6\text{NaNO}_3 + 2\text{CO}_2$. The bismuth subcarbonate is next re-dissolved in nitric acid to form normal bismuthous nitrate again: $(\text{BiO})_2\text{CO}_3 \cdot \text{H}_2\text{O} + 8\text{HNO}_3 = 2\text{Bi}(\text{NO}_3)_3 + 4\text{H}_2\text{O} + \text{CO}_2$. Finally the normal bismuthous nitrate is converted into subnitrate as follows: $\text{Bi}(\text{NO}_3)_3 + 2\text{NH}_3 + 2\text{H}_2\text{O} = \text{BiONO}_3 \cdot \text{H}_2\text{O} + 2\text{NH}_4\text{NO}_3$.

Notes.—The metal dissolves rapidly at first, but toward the last it is best to apply heat if economy of time is desired. Perforated baskets of stoneware are used for suspending the bismuth in the acid when bismuth preparations are prepared on a moderately large scale, the acid being placed in a stone pot and the basket containing the bismuth suspended just below the surface of the acid.

Unless the vessel in which the solution is effected is sufficiently large to obviate all risk and inconvenience from the violence of the reaction, the metal should be added in portions, each portion to be entirely dissolved before more is added. The capacity of the vessel ought to be about three times the combined volume of the acid and water used to dissolve the metal.

The strong solution can not be filtered through paper, for the acid liquid is so corrosive as to destroy the paper, not only defeating the filtration but also discoloring the solution. It is best to filter through coarsely powdered glass or glass wool, or washed asbestos; sometimes the solution is filtered through cotton previously immersed in dilute nitric acid. Decantation is the easiest method, and generally sufficient, especially when large quantities are operated upon. After dilution, however, filtration through paper is entirely practicable.

The object of first preparing subcarbonate of bismuth is to get rid of the arsenic which the metal contained. This arsenic is held in the acid solution as bismuth arsenate, nearly all of which precipitates upon dilution of the liquid with water, and is removed by filtration after standing twenty-four hours. The remainder of the arsenic is left in the last mother liquor as ammonium arsenate, together with the ammonium nitrate after precipitation of the subnitrate of bismuth with ammonia.

The character and composition of subnitrate of bismuth depend greatly upon the method of its preparation. Among the most important influences that affect the character of the product are these: The relative quantity of water used in the precipitation; the length of time the precipitate is exposed to the mother liquor; the amount and temperature of the water used for the precipitation; the quantity of water and the length of time consumed in washing; the use or omission of ammonia; and the greater or less care bestowed upon the various details of the process.

The process given above probably yields as uniform and satisfactory results as any. In order to insure success each step of the process should be carried out in strict accordance with the precise directions given.

In the Swedish Pharmacopœia the solution of bismuthous nitrate is evaporated to crystallization and the crystals afterward treated with a definite quantity of water. The evaporation must not be carried so far that a cake forms on the bottom of the dish, for then the salt will be hard and difficult to manage. The clear crystals removed from the mother liquor are carefully made dry by gently pressing them between blotting paper, which operation must be very carefully carried out so as not to soil the crystals with fibers from the paper. No heat must be used in drying the crystals. Triturate one part of the crystallized salt very thoroughly with four parts of distilled water, and then pour this mixture into a large vessel containing twenty-one parts of *boiling* distilled water, stirring constantly. Let cool; decant; and wash the precipitate on a strainer with ten parts of cold distilled water, gradually added. After draining as rapidly as possible, press out the last of the wash-water by means of a screw press, and dry the product on filter paper at not over 30° C. (86° F.).

In order to obtain a good product, the nitric acid used must be pure, distilled water must be used, and the acid solutions must not come in contact with wood or other organic substances, or with metals.

Whenever the precipitated subnitrate of bismuth is permitted to remain long in contact with the mother liquor in which it has been thrown down, it becomes more dense, and at the same time takes up more nitric acid. This must be avoided. Long contact with much water also renders the preparation heavier, but at the same time more basic. Cold liquids will yield a voluminous precipitate; hot water makes the precipitate more dense. If the water used for precipitating is 50° C. (122° F.) the precipitated subnitrate will have a composition corresponding to about 77 per cent. of Bi_2O_3 ; if the water is boiling hot (100° C.) the subnitrate will have a composition corresponding to about 80 to 81 per cent. of Bi_2O_3 . According to Loewe, the precipitate is not affected by a solution of ammonium nitrate, and hence it can be washed with such a solution without danger.

The precipitate must be dried at a low temperature (not over 30° C.), but must be thoroughly dry before it is put away. After removing all water that can be gotten rid of by pressing it, the precipitate should be dried in layers. If not thoroughly dried it decomposes by the influence of light and acquires a nitrous odor. If dried properly in layers, these can be easily broken and powdered by rubbing the pieces through a fine wire sieve by means of a soft brush. If dried

at too high a temperature the pieces are hard, not so readily powdered, and apt to yield a coarse, harsh powder.

Good subnitrate of bismuth is soft and bulky.

Tests.—When heated to redness, the salt gives off moisture, and afterward nitrous vapors, leaving a yellow residue which is soluble in nitric acid or hydrochloric acid, and which is blackened by hydrogen sulphide.

On dissolving 1 part of the salt with 5 parts of warm nitric acid (sp. gr. 1.200), no effervescence should occur (abs. of carbonate), and no residue should be left (abs. of insoluble foreign salts).

On boiling 1 Gm. of the salt with 10 C.c. of solution of soda (sp. gr. 1.260), and holding a glass rod dipped in acetic acid over the test tube, not more than a faint, white cloud, but no heavy, white fumes should appear (only traces of ammonia). If the preceding mixture, after thorough boiling, be diluted with water to 50 C.c., and filtered, the filtrate, when supersaturated with hydrochloric acid, and treated with hydrogen sulphide, should not deposit more than a trace of a precipitate, which should not have a yellow or orange color (only traces of antimony, arsenic, tin). On boiling 1 Gm. of the salt with 10 C.c. of strong solution of soda, decanting the liquid from the precipitated oxide of bismuth into a long test-tube, and adding about 0.5 Gm. of aluminium wire cut into small pieces (a loose plug of cotton being pushed a short distance down the tube), the generated gas should not impart any color or tint to paper wet with test solution of nitrate of silver and kept over the mouth of the test-tube for half an hour (abs. of more than traces of arsenic).

NORMAL BISMUTHOUS NITRATE.

BISMUTHI NITRAS.



Proceed as in the formula for making subnitrate of bismuth up to the point where the precipitated subcarbonate has been redissolved in nitric acid. Evaporate this solution to crystallization. Dry the crystals by gently pressing them between white filter paper, and at once put them in a glass stoppered bottle.

If copper is present the crystals have a bluish color.

The salt is in large, transparent crystals, colorless if pure. Decomposed by water; soluble in dilute nitric acid, and in glycerin.

GLYCERITE OF BISMUTH NITRATE.

GLYCERITUM BISMUTHI NITRATIS.

Normal bismuth nitrate	1 part.
Glycerin	8 parts.

Powder the crystals by trituration in a mortar. Then add the glycerin, all at once, and stir until the salt has dissolved.

Notes.—If the crystals are triturated *with* the glycerin, especially with a *small quantity* of glycerin, there is danger that nitro-glycerin may be formed and explosion result.

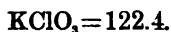
The solution is used for preparing certain other bismuth preparations by double decomposition, as the oleate, salicylate, and valerate.

NITRITES.

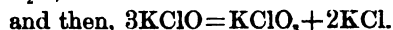
Of these salts potassium nitrite alone need be mentioned. It is a valuable reagent employed in the separation of cobalt, and is prepared by heating fused potassium nitrate with metallic lead, which takes part of the oxygen, or by saturating potassium hydrate solution with nitrous fumes evolved from nitric acid and starch. The nitrate formed is separated by crystallization.

CHLORATES.

The chlorates of potassium and sodium are the only ones employed, and both are water soluble, the sodium salt being more freely soluble than potassium chlorate.

POTASSIUM CHLORATE.**POTASSII CHLORAS.**

This useful salt was formerly prepared by saturating a solution of potassa with chlorine gas, whereby hypochlorite and chloride of potassium were formed, the hypochlorite being then decomposed by heat to form chlorate.



The chlorate crystallizes from the solution on cooling, while the chloride remains in the liquid.

Liebig's method, which is more recent and the one generally employed, consists in treating a mixture of calcium hydrate and potassium chloride, in solution, with chlorine gas, when the calcium chlorate formed, and the potassium chloride yield potassium chlorate and calcium chloride.

The product is liable to contain a little potassium and calcium chloride, which are eliminated by recrystallization.

It is purified and granulated as follows:

Potassium chlorate.....	1 part.
Boiling distilled water	5 parts.

Dissolve and filter. Stir constantly with a glass rod until cool. Collect the crystals on a filter, let drain, and then dry.

The mother liquor still contains about six per cent. of its weight of the salt, most of which may be recovered by evaporating the liquid at about 95° C. (203° F.) to one-third its bulk, stirring until cool, and collecting, draining, and drying the crystals as before.

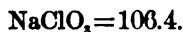
Description.—It crystallizes in thin glistening plates or short prisms; it is but sparingly soluble in cold water, but boiling water dissolves it in large quantities.

Tests.—Must be completely soluble in water, and the solution should yield no precipitate when treated with silver nitrate or barium chloride.

When strongly heated it should lose 39.2 per cent. of oxygen, and leave a residue which is completely precipitated by silver nitrate solution.

SODIUM CHLORATE.

SODII CHLORAS.



Prepared from calcium hydrate and sodium chloride with chlorine, or from chlorinated lime and sodium chloride, by a process analogous to that for preparing potassium chlorate.

It was formerly made as follows:

Tartaric acid.....	117 parts.
Sodium carbonate.....	110 parts.
Potassium chlorate.....	96 parts.

Dissolve the acid and the carbonate in 1,000 parts of hot water. To the hot solution add the potassium chlorate. Potassium bitartrate separates, and the solution contains the sodium chlorate together with some potassium bitartrate, which deposits during the evaporation to crystallization, the last portions being gotten rid of by crystallizing it out.

Description.—A crystalline salt much more soluble than potassium chlorate.

Tests.—These are similar to those employed for potassium chlorate. 106.4 parts when fused strongly should leave 58.4 parts of NaCl.

HYPOCHLORITES.

The following substances depend upon hypochlorites for their efficiency. Similar in behavior is the *Eau de Javelle*, which contains potassium hypochlorite, and is made by a process analogous to the one by which the "chlorinated soda" solution is obtained.

CHLORINATED LIME.**CALX CHLORATA.****[CHLORIDE OF LIME.]**

A compound resulting from the action of chlorine upon hydrate of calcium and containing at least 25 per cent. of available chlorine. By "available chlorine" is meant the amount of chlorine yielded by the preparation upon addition of an acid. It probably contains $\text{Ca}(\text{OCl})_2$. With water it yields hypochlorite and chloride of calcium.

Chlorinated lime should be preserved in well closed vessels, in a cool and dry place.

Description.—A white or grayish-white, dry, or but slightly damp powder, or friable lumps, becoming moist and gradually decomposing on exposure to air, having a feeble, chlorine-like odor, and a disagreeable saline taste. It is partially soluble in water and in alcohol. On dissolving chlorinated lime in diluted hydrochloric acid, chlorine gas is given off, and there should not remain more than a trifling amount of insoluble matter. Its solution in diluted acetic acid yields, with test solution of oxalate of ammonium, a white precipitate soluble in hydrochloric acid. The aqueous solution quickly destroys the color of a dilute solution of litmus or of indigo.

Tests.—If 0.71 Gm. of chlorinated lime be mixed with a solution of 1.25 Gm. of iodide of potassium in 120 C.c. of water, and 9 Gm. of diluted hydrochloric acid be then added, the red-brown liquid should require for complete decoloration not less than 50 C.c. of the volumetric solution of hyposulphite of sodium.

SOLUTION OF CHLORINATED SODA.**LIQUOR SODÆ CHLORATÆ.****[LABARRAQUE'S SOLUTION.]**

Sodium of carbonate.....	10 parts.
Chlorinated lime	8 parts.
Water, sufficient.	

Mix the chlorinated lime well with 40 parts of water in a tared vessel; cover it tightly. Dissolve the sodium carbonate in 40 parts of boiling water, and pour this hot solution into the solution of chlorinated lime. Cover the vessel tightly, let stand until cold, and then add enough water to make the whole weigh 100 parts. Finally, strain the liquid through muslin, allow the precipitate to subside, siphon off the clear solution, and keep it in a well stoppered bottle.

Reaction.— $\text{Ca}(\text{OCl})_2 + \text{CaCl}_2 + 2\text{Na}_2\text{CO}_3 = 2\text{NaOCl} + 2\text{NaCl} + 2\text{CaCO}_3$.

Notes.—The object of using hot solution of sodium carbonate is to produce a dense calcium carbonate, which settles more readily than a lighter precipitate. At the same time it should be remembered that high heat decomposes the hypochlorite of sodium formed, and the value of the preparation would then be impaired by loss of available chlorine. The new British Pharmacopœia does not prescribe hot water.

Keep the product in well stoppered bottles.

Description.—A clear, pale greenish liquid, of a faint odor of chlorine, a disagreeable and alkaline taste, and an alkaline reaction. Sp. gr. 1.044. Its specific volume is 0.958. Addition of hydrochloric acid causes an effervescence of chlorine and carbonic oxide gas. It rapidly decolorizes indigo, and produces a copious, light brown precipitate with solution of ferrous sulphate.

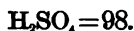
CHAPTER XVII.

SULPHATES.

Sulphate of lead and of barium, and basic mercuric sulphate, are insoluble. Sulphate of calcium dissolves in water to but a limited extent. The other sulphates are quite soluble.

SULPHURIC ACID.

ACIDUM SULPHURICUM.



The official sulphuric acid is required to contain not less than 96 per cent. of H_2SO_4 .

Crude sulphuric acid is prepared by oxidation of sulphurous acid by means of nitric acid in the presence of air and moisture.

It is commonly called "oil of vitriol," and usually contains arsenic, lead, iron, nitric acid, sulphurous acid, etc. When the acid is diluted with more than three times its weight of water the lead sulphate precipitates.

Commercial sulphuric acid should be nearly colorless, or but faintly yellowish. Usually it has the sp. gr. 1.835 corresponding to 66° B., and contains about 94 per cent. of absolute hydrogen sulphate.

Purification.—A mixture of 800 parts of crude commercial sulphuric acid and 1 part of ammonium sulphate is distilled from a retort by gradually increased heat over the naked fire. The mixture is slowly raised to the boiling point, and the first 15 parts, containing chiefly water and sulphurous acid, are rejected, after which the next 225 parts are collected.

The object of adding the ammonium sulphate is to remove nitrogenous compounds by decomposition.

Properties.—Colorless, oily, inodorous, highly corrosive, charring or blackening organic substances by abstracting the elements of water. The specific gravity should not be below 1.840, corresponding to 66°.3 B. It contains at least 96 per cent. of H_2SO_4 , corresponding to 80 per cent. of sulphuric anhydride. When mixed with water or with alcohol chemical action takes place, there is considerable heat evolved, and a contraction of volume results. Neither water nor alcohol should be poured into strong sulphuric acid; but when such mixtures are to be made the acid should be added slowly to the water or to the alcohol, as the case may be, to prevent accident from spurting caused by the sudden boiling of the mixture. The heat is caused by the chemical action; when the acid is mixed with water hydrates are formed, and when it is mixed with alcohol ether is produced.

Relation of weight to volume.—The specific gravity being 1.840, its specific volume is 0.543. The usual half gallon acid bottle holds 9 pound-avoirdupois.

Action on metals.—Dissolves most metals to form sulphates. Lead, however, is scarcely attacked.

Tests.—The Pharmacopœial tests require an acid free from arsenic, nitric acid, and sulphurous acid. In other words, no acid below the grade commercially designated as "C. P." is sufficiently pure.

Saturating power.—See the table under the title, Diluted Sulphuric Acid (10 per cent. H_2SO_4).

Specific Gravity and Percentage Strength of Solutions of H_2SO_4 .
(Bineau.)

Per cent. of H_2SO_4 .	Sp. gr. 15°.	Per cent. of H_2SO_4 .	Sp. gr. 15°.
1	1.0064	21	1.1516
2	1.0120	22	1.1590
3	1.0190	23	1.1670
4	1.0256	24	1.1740
5	1.0320	25	1.1820
6	1.0390	30	1.2230
7	1.0464	35	1.2640
8	1.0536	40	1.3060
9	1.0610	45	1.3510
10	1.0680	50	1.3980
11	1.0756	55	1.4480
12	1.0830	60	1.5010
13	1.0910	65	1.5570
14	1.0980	70	1.6150
15	1.1060	75	1.6750
16	1.1136	80	1.7340
17	1.1210	85	1.7860
18	1.1290	90	1.8220
19	1.1360	95	1.8376
20	1.1440	100	1.8426

Strength.—The U. S. Pharmacopœia permits the use of any sulphuric acid containing 96 per cent. or over of absolute H_2SO_4 . The German Pharmacopœia allows the use of an acid of from 1.836 to 1.840 sp. gr., containing 94 to 96 per cent. of absolute hydrogen sulphate. The French Pharmacopœia prescribes the sp. gr. 1.840. The British Pharmacopœia prescribes an acid of 1.843 sp. gr., containing 98 per cent. of H_2SO_4 .

DILUTED SULPHURIC ACID.

ACIDUM SULPHURICUM DILUTUM.

Sulphuric acid..... 1 part.
Distilled water..... 9 parts.

Pour the acid gradually, with constant stirring, into the water.

Keep the product in glass stoppered bottles.

Description—A colorless liquid, having a specific gravity of 1.067 at 15° C.; its sp. vol. is 0.987.

It is completely volatile when heated on platinum foil.

Tests.—Should be free from traces of nitric acid as shown by test with solution of ferrous sulphate, from traces of hydrochloric acid as shown by test with solution of silver sulphate, from traces of heavy metals as shown by test with hydrogen sulphide.

Zinc should dissolve in it, liberating pure hydrogen free from hydrogen sulphide or arsenide, as shown by the reaction with lead paper and with the Marsh test.

To neutralize 10 C.c., 21.8 C.c. of the normal sodium hydrate solution should be required.

Saturating power.—100 parts of diluted sulphuric acid, containing 10 per cent. of H_2SO_4 , will saturate:

Potassa (100 per cent. KOH), 11.43 parts.....	} Yielding 17.75 parts of potassium sulphate
Potassa (90 per cent.), 12.70 parts.....	
Solution of potassa (5 per cent.), 228.60 parts.....	
Potassium carbonate (81 per cent.), 17.88 parts.....	
Potassium carbonate (100 per cent.), 14.06 parts.....	
Potassium bicarbonate, 20.41 parts.....	
Soda (100 per cent. NaOH), 8.16 parts.....	} Yielding 32.86 parts of sodium sulphate.
Soda (90 per cent.), 9.07 parts.....	
Solution of soda (5 per cent.), 163.26 parts.....	
Sodium carbonate (96 per cent.), 30.40 parts.....	
Sodium carbonate (100 per cent.), 29.18 parts.....	
Sodium bicarbonate (99 per cent.), 17.14 parts.....	
Sodium bicarbonate (100 per cent.), 17.31 parts.....	
Ammonia (NH_3), 8.469 parts.....	} Yielding 12.65 parts of ammonium sulphate.
Ammonia water (10 per cent.), 84.69 parts.....	
Ammonia water, stronger (28 per cent.), 12.89 parts.....	
Ammonium carbonate, 10.68 parts.....	

AROMATIC SULPHURIC ACID.

ACIDUM SULPHURICUM AROMATICUM.

Sulphuric acid	40	parts.
Tincture of ginger	9	parts.
Oil of cinnamon	0.20	parts.
Alcohol, sufficient.		

Add the acid gradually to 140 parts of alcohol, and let the mixture cool. Then add the tincture and the volatile oil, and finally enough alcohol to make the total product weigh 200 parts.

Should be preserved in glass stoppered bottles.

Notes.—By the action of the sulphuric acid on the alcohol, ethyl-sulphuric acid and ether are formed. The preparation consequently contains sulphuric acid, alcohol, ether, and ethyl-sulphuric acid in addition to the aromatics, which are also modified and partly decomposed by the strongly acid liquid.

Formerly this preparation was made by mixing a compound tincture of ginger and cinnamon with sulphuric acid and alcohol. The larger quantity of organic substances contained in the product so obtained caused the continuous formation

of sediment by the action of the sulphuric acid. In the present preparation this difficulty is to some extent avoided. The old aromatic sulphuric acid was very dark, brownish red, and contained more ginger and less cinnamon than the new, which is of a much lighter reddish brown color.

Description.—Has 0.955 sp. gr., and contains about 20 per cent. of official sulphuric acid. Its sp. vol. is 1.047.

Tests.—9.8 Gm. diluted with 20 volumes of water, and filtered, should require for complete neutralization not less than 86 C.c. of the normal solution of soda.

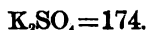
HALLER'S ACID DROPS.

LIQUOR ACIDUS HALLERI.

This is a mixture of equal parts by weight of alcohol and sulphuric acid. The acid must be added to the alcohol gradually and cautiously, with constant stirring, in order that the temperature may not rise so high as to cause the liquid to boil. The liquid contains alcohol, sulphuric acid, ether, and ethyl-sulphuric acid. If the alcohol was pure, the preparation is colorless.

POTASSIUM SULPHATE.

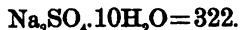
POTASSII SULPHAS.



This salt is prepared by the action of sulphuric acid on potassium chloride. Its solution in water is used as a reagent for the detection of strontium.

SODIUM SULPHATE.

SODII SULPHAS.



Obtained as a by-product in the preparation of the phosphates of iron, and in several other processes.

CARLSBAD SALT.

SAL CARLSBADENSE FACTITUM.

Sodium chloride	1 part.
Sodium bicarbonate	2 parts.
Sodium sulphate	50 parts.

The chloride and the bicarbonate must be well dried, separately, and then powdered. The sulphate, in crystals, should also be powdered separately, which can hardly be effected otherwise than by granulating the previously dissolved salt. If dried sodium sulphate is used, the product will yield hard lumps when water is added, and these hard particles dissolve but slowly.

Notes.—This preparation differs from the natural Carlsbad salt in that the latter contains also some potassium sulphate. It should be kept in tightly corked bottles in a cool place. After long keeping, however, it acquires a disagreeable odor, reminding of lye.

A white crystalline powder, readily soluble in water.

AMMONIUM SULPHATE.

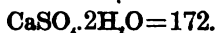
AMMONII SULPHAS.



Obtained as a by-product in preparing ferric hydrate and in several other processes. It may also be made by neutralizing diluted sulphuric acid with water of ammonia, filtering, and evaporating to crystallization or granulation. One hundred volumes of diluted sulphuric acid (10 per cent.) will require about 40 volumes of official water of ammonia.

CALCIUM SULPHATE.

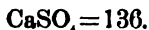
CALCHII SULPHAS.



This salt is but very sparingly soluble in water. The solution is sometimes employed as a reagent in the laboratory.

DRIED CALCIUM SULPHATE.

CALCHII SULPHAS USTUS.



When calcium sulphate is deprived of its water by heating it to between 100° and 200° C. (212° to 392° F.) it is converted into so-called *plaster of Paris*, which is anhydrous calcium sulphate. This, when mixed with enough water to form a thin paste, hardens in a few minutes, and hence its use for castings, bandages, etc.

MAGNESIUM SULPHATE.**MAGNESII SULPHAS.**

[EPSOM SALT.]



A solution of this salt containing ammonium chloride and hydrate is a valuable reagent for the detection of phosphates and arsenates.

The crystals lose water in dry air and become anhydrous by application of strong heat.

The solution in water should be perfectly clear, and should not be precipitated by ammonium sulphide nor by ammonium hydrate or carbonate after addition of ammonium chloride solution.

DRIED MAGNESIUM SULPHATE.**MAGNESII SULPHAS EXSICCATUS.**

At 30° to 52° C. (86° to 126° F.) the crystallized magnesium sulphate loses 1 molecule of water of crystallization, and 4 additional molecules of water are expelled by drying the salt by water-bath heat.

The product is a white powder, which readily absorbs moisture from the air, and, therefore, must be kept in tightly closed bottles.

ZINC SULPHATE.**ZINCI SULPHAS.**

[WHITE VITRIOL.]



Zinc clippings, or granulated zinc.....	4 parts.
Sulphuric acid	5 parts.

Dilute the acid with 30 parts of water; add the zinc gradually. When effervescence has ceased, digest with the undissolved portion of the metal for a few days. Filter. Evaporate the filtrate until a drop becomes turbid on cooling. Then let the solution become cold, stirring constantly so that small crystals may be formed. Collect and dry these on muslin. Evaporate the mother liquor to obtain more crystals.

Reaction.— $\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2$.

Notes.—The zinc should be nearly free from other metals. If it contains iron, the zinc sulphate contaminated with ferrous sulphate will become yellow in time by the oxidation of the ferrous to ferric salt. Zinc sulphate containing iron will, of course, be unfit for the preparation of zinc oxide.

Any iron and manganese present in the metal will not be removed by digestion with an excess of zinc; but lead, copper, and cadmium, if present, are thus separated. The gray flocculi which are formed when the zinc is dissolved in the acid are mainly lead.

Pure zinc dissolves with difficulty in the acid; if it contains iron it dissolves more rapidly in proportion to the iron in it.

The solution should not be too concentrated for crystallizing, for when the salt is crystallized from a warm solution (over 30°C .) the crystals formed contain less water of crystallization ($\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$). The crystals should be dried without the aid of heat, or at least at a temperature not exceeding 30°C . (86°F .)

Impure zinc sulphate may be purified to a great extent by recrystallization. The salt crystallizes best from a slightly acid solution.

Zinc sulphate may also be made by saturating sulphuric acid with zinc oxide and crystallizing.

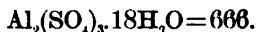
Description.—Small, colorless crystals, very soluble in water, and insoluble in alcohol.

They have a sharp metallic taste and effloresce in dry air. At a high temperature all of the water of crystallization may be expelled.

Tests.—The solution in water should give a perfectly white precipitate with ammonium sulphide. It should be precipitated white by ammonium hydrate, and be completely dissolved when excess is added, showing absence of iron and aluminium compounds.

ALUMINIUM SULPHATE.

ALUMINII SULPHAS.



Alum	30 parts.
Sodium carbonate	28 parts.
Sulphuric acid	9 parts.

Dissolve the alum and the sodium carbonate, each in 400 parts of boiling water, filter, and pour the hot alum solution into the hot solution of sodium carbonate, stirring constantly. Digest the mixture at a gentle heat until the evolution of carbon dioxide ceases. Wash the precipitate with hot water until the washings no longer yield a precipitate with test solution of barium chloride. Then let the precipitated aluminium hydrate drain as far as possible, and dissolve it with the aid of gentle heat in the sulphuric acid, previously diluted with 50 parts of water; filter the solution, evaporate it until a pellicle begins to form, and then continue the evaporation with constant stirring, over a water bath, until a nearly dry white salt remains.

For reactions and notes see under title, Aluminium Hydrate.

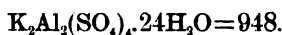
Description.—A white powder with a peculiar sweetish astringent taste. Readily soluble in water, but nearly insoluble in alcohol.

Tests.—Should yield a flocculent perfectly white precipitate with ammonium hydrate. .666 Gm. dissolved in water, and precipitated as above, gives a precipitate which when washed, dried, ignited and weighed, should amount to .103 Gm.

In precipitating, only a slight excess of ammonia water must be added, and the solution boiled.

POTASSA ALUM.

ALUMINII ET POTASSII SULPHAS.



This serves as the material for the preparation of several other aluminium compounds.

Description.—Large colorless crystals, with sweetish astringent taste, soluble in water, insoluble in alcohol.

Tests.—When strongly heated the crystals should lose 45.57 percent. of their weight (water). A solution of the crystals in water should not be colored blue on addition of potassium ferrocyanide.

From an aqueous solution sodium or potassium hydrate throws down a bulky white precipitate of aluminium hydrate, soluble in excess. Ammonia produces the same precipitate, which is nearly insoluble in excess of this reagent. The filtrate from this should not be precipitated by ammonium sulphide.

GRANULATED ALUM.

ALUMEN TURBIDATUM.

Alum	20 parts.
Diluted sulphuric acid	1 part.
Boiling water	40 parts.

Dissolve the alum in the boiling water, add the acid and mix well, filter while hot, and let the filtrate cool, stirring it constantly until cold. Collect and dry the crystals.

GLYCERITE OF ALUM.

GLYCERITUM ALUMINIS.

Alum, in fine powder	4 Gm.
Glycerin	20 C.c.

Stir them together in a porcelain capsule, and heat gently over a water-bath until dissolved. Set aside; decant the clear liquid from any deposit which may have formed.

DRIED ALUM.**ALUMEN EXSICCATUM.**

Expose 11 parts of alum, for several days, to a temperature of about 89° C. (176° F.) until it has thoroughly effloresced. Then heat it in a porcelain dish gradually up to 200° C. (392° F.), taking care not to permit the temperature to rise above 205° C. (400° F.), and continue the heating until a porous white mass remains, weighing 6 parts.

When cold, powder it, and keep it in well closed bottles.

Notes.—Potassa alum contains 45.57 per cent. of water of crystallization. When heated to 40° C. (104° F.) it loses about 2.7 per cent. of water; at 47° C. (116.6° F.) it loses 9.6 per cent.; at 60° C. (140° F.) it loses most of its water of crystallization, but the crystals still retain to a great extent their form, and the product, which is not porous, yields a clear solution with water. At 80° C. (176° F.) the salt effloresces completely, but still retains a considerable amount of water. Long continued drying at 100° C. (212° F.) expels all of the water and leaves a product which is entirely soluble in water. When heated at once above 92° C. (197.6° F.) potassa alum dissolves in its water of crystallization, and the liquid solidifies only after long standing. When gradually heated, as prescribed in the Pharmacopœial working formula, and finally to a temperature between 200° and 205° C., all the water having thus been expelled without liquefying the alum, the product is light and porous. Should the heat be too low, a glassy mass may be obtained which cannot afterwards be rendered porous; in this glassy condition the alum is said to retain 14 molecules of water.

A common flower-pot of clay is very suitable for the exsiccation of alum. Alum in whole crystals may also be very successfully dried on hot iron plates, a porous product free from water being thus easily prepared. The surface in contact with the iron will, however, be found more or less discolored, and next to this discolored surface will be found a thin glassy crust, all of which must be scraped off with a knife, leaving a perfectly satisfactory product.

During the process of heating the alum there is considerable swelling and foaming from the watery vapors, toward the close. Hence the dish or pot used should be only about one-fourth to one-third filled. During the heating the alum is not to be stirred.

Dried alum should be kept in tightly closed bottles. Exposed to a moist atmosphere it absorbs water quite rapidly, even to the extent of 18 molecules, or over 50 per cent. of its weight.

Description.—A white powder, soluble in water, insoluble nearly in alcohol.

Tests.—The solution in water gives a pure white precipitate with ammonia water, and is not colored by ammonium sulphide.

FERROUS SULPHATE.**FERRI SULPHAS.**

On a large scale crude ferrous sulphate or "copperas" is made by roasting iron pyrites, the mass being afterwards leached out with water acidulated with sulphuric acid. Sulphate of iron is also obtained as a

by-product in the process of galvanizing iron wire, the bath of dilute sulphuric acid employed to clean the wire becoming finally saturated by the metal.

Among the impurities present in "green vitriol," or "copperas," are manganese, zinc, copper, aluminium, etc.

A good grade of copperas is one free from dirt, and consisting mostly of clear, or nearly clear, bluish-green crystals. The large, clear, crystals are the purest. Efflorescence on the surface of the crystals is common. When the salt is covered with yellow or brownish basic ferric salt, the copperas is of poor quality. A bluish tint is indicative of freedom from ferric salt; an opaque green color, without any bluish cast, points to oxidation.

A solution of common copperas in water is unclear. It may be rendered clear by heating to the boiling point, adding a small quantity of sulphuric acid, and filtering. The commercial article may be greatly improved by this means, the purified salt being recrystallized from the bright bluish-green solution.

Description.—Clear green crystals, which oxidize quickly on exposure to air. Readily soluble in water, insoluble in alcohol.

Tests.—The solution acidified with hydrochloric acid should not be colored by hydrogen sulphide.

The pure salt contains 20.14 per cent. of iron, which can be determined by use of standard solution of KMnO_4 , as given under Volumetric Analysis.

Pure ferrous sulphate may be made as follows:

Iron wire	200 Gm.
Sulphuric acid	200 C.c.
Water	1,500 C.c.

Pour the water on the iron in a porcelain dish, add the acid, and, when effervescence has ceased, boil for ten minutes. Filter. Set the filtrate aside for twenty-four hours. Then collect the crystals of ferrous sulphate, dry them on filter-paper placed on porous bricks. Upon evaporation the mother liquor yields a second crop of crystals.

Reaction.— $\text{Fe} + \text{H}_2\text{SO}_4 = \text{FeSO}_4 + \text{H}_2$.

Notes.—The iron is used in excess of amount required by theory in order that no ferric salt may be formed. The hydrogen, which is liberated in the chemical reaction, has a disagreeable odor from volatile carbon, sulphur, and phosphorus compounds usually present.

To still further prevent contamination with ferric salt, the filtrate may be acidulated with sulphuric acid before being set aside to cool; any ferric sulphate present will remain in the mother liquor.

The crystals should be dried as rapidly as practicable to avoid oxidation, which easily takes place when the salt is moist. To facilitate the drying the crystals may be hastily washed with a little alcohol, which evaporates rapidly.

The solution of ferrous sulphate can also be filtered into alcohol, in which the salt is insoluble, as prescribed in the process of the U. S. Pharmacopœia for making

PRECIPITATED FERROUS SULPHATE.**FERRI SULPHAS PRÆCIPITATUS.**

Ferrous sulphate	500 Gm.
Hot distilled water	650 C.c.
Diluted sulphuric acid	200 C.c.
Alcohol	1,000 C.c.

Dissolve the sulphate in the water previously mixed with the acid. Filter while hot. Let the filtrate cool, and then pour it gradually, during constant stirring, into the alcohol. Set the mixture aside a few hours, in a well covered vessel. Collect the crystals on a filter, wash them with alcohol until the washings no longer reddens blue litmus paper, and then let the mass be well drained. Fold the salt between bibulous paper, with gentle pressure, and finally expose it to a current of air, stirring it frequently until quite dry. Put the product in well stoppered bottles.

Notes.—Ferrous sulphate is insoluble, but ferric sulphate is soluble, in alcohol. The presence of any ferric salt renders the color of the ferrous sulphate a nearly pure green, whereas a product free from ferric sulphate is bluish green. Precipitated sulphate of iron is in very small crystals, and is sometimes designated as “granulated sulphate of iron,” although the latter title more properly belongs to a preparation made in a manner analogous to the process given for making granulated alum.

Description.—A pale green powder, corresponding in general properties to the large crystals.

Tests.—Usually purer than the large crystals, but the same in general reactions.

DRIED FERROUS SULPHATE.**FERRI SULPHAS EXSICCATUS.**

Crystallized ferrous sulphate contains 7 molecules of water. When moderately heated it dissolves in its water of crystallization; between 33° C. (91°.4 F.) and 90° C. (194° F.) the salt loses 6 molecules of that water, but the seventh molecule of water is not expelled until the heat is raised to 280° C. (536° F.), at which temperature partial decomposition of the sulphate is liable to take place. The Pharmacopœial “dried sulphate of iron” is ferrous sulphate with one molecule of water.

In exsiccating ferrous sulphate, liquefaction of the salt, by solution in its water of crystallization, must be avoided if a light-colored product, unoxidized and free from hard particles, is to be obtained. The ferrous sulphate should be pure, and granulated, precipitated, or

otherwise reduced to coarse powder. It may then be spread out in a thin layer on paper and be placed in a drying room where the temperature is about 40°C . (104°F). The drying may also be effected by the heat of the sun until thoroughly effloresced, or converted into a white powder. Occasional stirring is required. Should the temperature exceed 50°C . the salt partly dissolves in its water of crystallization and the liquid penetrates the paper. Delf plates may be used instead of paper, or porcelain or iron dishes. If the salt is allowed to become so hot as to dissolve in its water of crystallization, it will oxidize more rapidly, and becomes discolored. After having effloresced, however, it will no longer liquefy even at water-bath heat, or higher temperatures. If water-bath heat is used in finishing the exsiccation, several days' heating will be necessary to expel the last portions of the sixth molecule of water; but an almost white product may readily be obtained, amounting to about 64 to 65 per cent. of the crystallized salt, without prolonging the heating over water-bath beyond a few hours, the powder being well stirred during the process. To get rid of the remainder of the sixth molecule of water it is necessary to raise the heat to about 120° to 150°C . (248° to 302°F .), continuing the heat until the product ceases to lose weight. This prolonged exposure inevitably results in a dark-colored product.

One Gm. of dried ferrous sulphate corresponds to $1\frac{1}{2}$ Gm. of the crystallized salt.

Description.—A grayish white powder, which leaves a slight residue on treatment with water; insoluble in alcohol.

Tests.—As for the crystals. When tested with solution of KMnO_4 , the salt should be found to contain 32.9 per cent. of iron.

SOLUTION OF NORMAL FERRIC SULPHATE.

LIQUOR FERRI TERSULPHATIS.

[SOLUTION OF TERSULPHATE OF IRON.]

An aqueous solution of normal ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$, 400), containing 28.7 per cent. of that salt.

Ferrous sulphate	80 parts.
Sulphuric acid	15 parts.
Nitric acid, sufficient.	

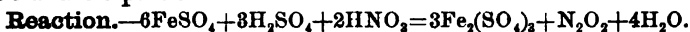
The ferrous sulphate is to be in a coarse powder. Its oxidation is effected in a porcelain dish capable of holding at least twice the quantity of final product to be made.

Put fifty parts of distilled water in the boiling dish; to this add gradually the sulphuric acid, and afterwards eleven parts of nitric acid. Place the vessel under a hood so arranged that the gas escaping from the liquid will pass out through a flue. Heat the liquid to the boiling point and then add the ferrous sulphate gradually, waiting after each addition until effervescence has ceased before adding the next portion, and stirring the mixture constantly.

When all the ferrous sulphate has been added, test the solution for ferrous salt. Upon adding a few drops of it to freshly prepared test-solution of ferricyanide of potassium there will be no blue coloration nor any precipitate if ferrous sulphate is absent. In that case the solution is to be heated until free from nitrous odor.

Should the presence of ferrous salt be revealed by the test, add more nitric acid, drop by drop, to the hot liquid so long as it causes red fumes to be evolved. Continue heating the solution until it acquires a reddish brown color and is free from ferrous salt, as ascertained by the ferricyanide of potassium test, which should at most produce a greenish brown discoloration. Should the solution then have a nitrous odor, boil the liquid briskly until this disappears.

Finally add enough distilled water to make the whole product weigh two hundred parts.



Notes.—The oxidation of ferrous sulphate to ferric sulphate by nitric acid takes place much below 100°C . (212°F). Water-bath heat is, therefore, sufficient for this purpose. The process is, however, hastened by the application of a somewhat higher degree of heat.

To oxidize all the ferrous salt is not difficult, a sufficient amount of nitric acid being used. But the preparation must be free from nitric acid when finished, and it is extremely difficult to expel the excess which is almost always added in order to complete the oxidation. Sometimes it is directed to boil down the solution to dryness, and to redissolve the tough mass in water; but even this precaution fails to remove all traces of nitric acid. Hence, great care should be taken not to use more nitric acid than is necessary.

Uses.—For making ferric hydrate and various other ferric compounds.

Description.—A dark reddish brown solution, with acid and styptic taste and reaction. Mixes readily with alcohol. Its sp. gr. is 1.320, and its sp. vol. 0.758.

Tests.—When tested with potassium ferricyanide a blue color should not appear. The solution should be completely precipitated by ammonia water, yielding red ferric hydrate. Nitric acid or nitrous compounds must be absent, as shown by test with crystal of ferrous sulphate and sulphuric acid.

SOLUTION OF BASIC FERRIC SULPHATE.

LIQUOR FERRI SUBSULPHATIS.

[SOLUTION OF SUBSULPHATE OF IRON. MONSIEUR'S SOLUTION.]

An aqueous solution containing 43.7 per cent. of basic ferric sulphate ($\text{Fe}_2\text{O}(\text{SO}_4)_3$, 720).

Ferrous sulphate	77 parts.
Sulphuric acid	7 parts.
Nitric acid, sufficient.	

Put 50 parts of distilled water in a boiling dish of porcelain. Add the sulphuric acid, and then eleven parts of nitric acid. Heat the mixture to the boiling point, or near it, and then add the ferrous sulphate, in coarse powder, a small portion at a time, waiting after each addition until the effervescence has ceased before adding more.

The boiling dish should be large enough to hold at least twice the amount of product to be made, and the oxidation must be done in the open air, or under a fume hood, where the nitrous vapors evolved will be carried off through a flue.

Should the addition of a few drops of nitric acid cause further evolution of red fumes after all of the ferrous sulphate has been added, more nitric acid is to be cautiously added until red vapors cease to be given off. Then keep the solution boiling briskly until nitrous vapors are no longer perceptible and the liquid assumes a ruby-red color. Finally add enough water to make the whole weigh 114 parts.

Reaction.— $12\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 + 2\text{HNO}_3 = 3(\text{Fe}_2\text{O}(\text{SO}_4)_3) + \text{N}_2\text{O}_2 + 4\text{H}_2\text{O}$.

Notes.—Compare with the remarks under Ferric Hydrate and under Solution of Normal Ferric Sulphate. This solution has the sp. gr. 1.555 and the sp. vol. 0.643.

BASIC FERRIC SULPHATE.

FERRI SUBSULPHAS.

[SUBSULPHATE OF IRON. MONSIEUR'S SALT.]



When solution of basic ferric sulphate is evaporated at a moderate heat upon a delf or glass plate, the residue consists of transparent scales, which deliquesce on exposure. When dried at a higher temperature, the salt turns yellow and becomes less hygroscopic. When the solution is painted upon an iron plate with a brush, and the plate heated over a naked flame, the residue is a light yellow porous crust, which should be at once removed, and powdered while still hot in a warm mortar. The product thus obtained is lemon yellow, quite hygroscopic, and perfectly uniform.

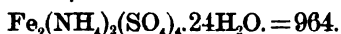
If the solution is evaporated to dryness in a dish, stirring the drying mass, and continuing the heat until a dry powder is formed, the product is a coarse, grayish-yellow, gritty powder, not readily soluble in water.

Monse's powder should be a fine, lemon yellow, hygroscopic powder. It must be kept in a tightly corked bottle.

AMMONIO-FERRIC ALUM.

FERRI ET AMMONII SULPHAS.

[SULPHATE OF IRON AND AMMONIUM. IRON ALUM.]



Solution of normal ferric sulphate	300 C.c.
Ammonium sulphate	40 Gm.
Diluted sulphuric acid	30 C.c.

Heat the iron solution to the boiling point; add the ammonium sulphate, and, when this has dissolved, add the acid. Stir well. Set the mixture aside in a well covered vessel, in a cool place, for a day or two. Remove the crystals from the mother liquor, wash them hastily with a little cold water, dry them at once by pressing them gently between blotting paper, and put them, without delay, in a bottle, which must be tightly stoppered and kept in a cool place.

The crystals should be clean, clear, well developed, and of a handsome violet color.

Reaction.— $\text{Fe}_2(\text{SO}_4)_3 + (\text{NH}_4)_2\text{SO}_4 + 24\text{H}_2\text{O} = \text{Fe}_2(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$.

Notes.—The small quantity of sulphuric acid is added, because good crystals are best obtained when a slight excess of acid is present. Should the solution of ferric sulphate contain free acid, the addition of the diluted sulphuric acid is unnecessary. If there is a deficiency of acid the crystals will be brownish, unclear, or very pale.

Description.—A violet colored salt, resembling alum in crystalline form, insoluble in alcohol, readily soluble in water, giving a brown solution.

Tests.—The absence of alumina should be shown by boiling the solution with potassium hydrate in excess, filtering, and heating the filtrate with solution of ammonium chloride; a gelatinous precipitate of aluminium hydrate should not appear.

The solution acidified with nitric acid should not yield a white precipitate when treated with silver nitrate, showing absence of chlorides.

MANGANOUS SULPHATE.

MANGANI SULPHAS.

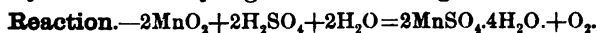


Black oxide of manganese, sulphuric acid, each sufficient.

The oxide, in fine powder, is mixed with sufficient sulphuric acid to form a thin paste; the mixture is heated to boiling, and the heating

continued until a dry residue remains ; this is transferred to a crucible and heated a few minutes at a dull red heat. It is then allowed to cool, water is added, and the solution filtered, and evaporated to crystallization.

The heating is to decompose any sulphate of iron which may be present. Should iron be present in the solution of manganous sulphate, it may be removed by digestion with manganous carbonate.



Description.—A pink or light rose-red crystalline salt, soluble in water, insoluble in alcohol.

The amount of water in the molecule depends on the temperature at time of crystallization.

Tests.—The acidified solution should not be colored black by hydrogen sulphide, nor blue by potassium ferrocyanide, showing absence of copper and iron. The solution should yield a flesh-colored precipitate when treated with ammonium sulphide.

COPPER SULPHATE.

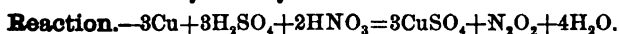
CUPRI SULPHAS.



This is usually prepared from the residues of copper-smelting works, containing sulphide or oxide. These residues are digested in leaden vessels with diluted sulphuric acid, and the solution of sulphate formed is evaporated to crystallization. Sometimes the sulphide is allowed to oxidize in the moist air, whereby sulphate is produced. On a small scale the following method may be employed:

Copper, in filings	5 parts.
Sulphuric acid	8 parts.
Nitric acid	4 parts.
Water	30 parts.

Mix the ingredients in a flask and heat at first gently, and afterwards raise the temperature gradually to the boiling point. Boil until the evolution of gas ceases, evaporate the solution to dryness, dissolve the residue in four times its weight of water, filter and evaporate to crystallization. Dry the crystals without the aid of heat.



Description.—Deep blue crystals, which lose water when heated, leaving a white anhydrous residue. Soluble in water, insoluble in alcohol.

Tests—The crystals frequently contain small amounts of ferrous sulphate. To detect this a solution is made and treated with chlorine or nitric acid to oxidize the iron. On saturating now with ammonium hydrate the latter precipitates as reddish hydrate from the deep blue solution.

A solution of copper sulphate, slightly acidified with hydrochloric acid, should be completely precipitated by hydrogen sulphide.

Granulated sulphate of copper.—Sulphate of copper, reduced to coarse powder, is dissolved in an equal weight of boiling water, and the solution filtered and evaporated during constant stirring until nearly dry, after which the residue is dried by spreading it in thin layers on paper and exposing it to currents of dry air.

Precipitated sulphate of copper may be made by dissolving the salt in its own weight of boiling water, and filtering the solution into an equal volume of alcohol.

AMMONIATED COPPER.

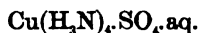
Copper sulphate	6 Gm.
Ammonium carbonate	8 Gm.

Triturate together until effervescence has ceased. Keep the product in a tightly-corked bottle.

Notes.—This preparation is similar in composition to the crystalline ammoniacal copper sulphate, which is more uniform, of handsome appearance, and prepared as follows:

AMMONIACAL COPPER SULPHATE.

CUPRI SULPHAS AMMONIACALIS.



Copper sulphate, in powder	100 Gm.
Ammonia water	300 C.c.
Alcohol	600 C.c.

Dissolve the sulphate of copper in the ammonia water contained in a porcelain capsule, without applying heat. (Heat is generated by the chemical solution.) When the liquid has become cold, filter it and put it into a wide-mouthed bottle of the capacity of 1,000 to 1,200 C.c. Then tilt the bottle a little to one side and pour the alcohol slowly and carefully into it, letting it run down along the side of the bottle so as not to mix with the solution but to form a separate stratum above it. Set it aside, without disturbing it, and well corked, for one or two days, and then decant the mother liquor, and throw it away. Collect the crystals and dry them as rapidly as possible without the aid of heat by gently pressing them between bibulous paper, avoiding exposure to the air as far as practicable. Put the product at once into a bottle and cork it tightly.

Description.—The preparation is in handsome, dark-blue, needle-like crystals, having an ammoniacal odor and a nauseous metallic taste. Soluble in 1.5 parts of water.

It is not "ammonio-copper sulphate," which may be made by mixing solutions of the sulphates of ammonium and of copper.

Ammoniacal copper sulphate readily absorbs oxygen from the air, and hence acts as an oxidizing agent on substances present in its solution. Thus, sodium thiosulphate is rapidly converted into sulphate; asparagin and glycocoll to oxalic and carbonic acids, etc.

ALUMINATED COPPER SULPHATE.

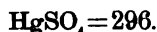
LAPIS DIVINUS.

Copper sulphate	15 parts.
Alum	15 parts.
Potassium nitrate	15 parts.
Camphor	1 part.

Powder the salts and mix them; fuse them together in a porcelain capsule; let the mass cool, powder it, and then incorporate the camphor.

MERCURIC SULPHATE.

HYDRARGYRI SULPHAS.



Mercury	500 Gm.
Sulphuric acid	300 C.c.

Heat them together in a porcelain capsule, stirring constantly, until the metal disappears and a dry white salt remains.

Reaction.— $\text{Hg} + 2\text{H}_2\text{SO}_4 = \text{HgSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$.

Notes.—Mercury is insoluble in cold sulphuric acid.

Mercuric sulphate is used in the preparation of calomel, corrosive sublimate, and basic mercuric sulphate.

Description.—A white powder, which forms with a small amount of water a crystalline salt, $\text{HgSO}_4 \cdot \text{H}_2\text{O}$. An excess of water converts it into yellow basic salt.

Tests.—Decomposes by heat, giving off SO_2 . At high temperature completely volatile.

BASIC MERCURIC SULPHATE.

HYDRARGYRI SUBSULPHAS FLAVUS.

[YELLOW SUBSULPHATE OF MERCURY. TURPETH MINERAL.]



Mercury	10 parts.
Sulphuric acid	5 parts.
Nitric acid	4 parts.
Distilled water, sufficient.	

Put the mercury in a roomy flask, add the sulphuric acid, and then the nitric acid, previously mixed with 3 parts of distilled water. Digest the mixture at a gentle heat until red fumes cease to be given off. Transfer the mixture to a porcelain dish and heat it on a sand-bath, with frequent stirring, until a dry, white salt remains. Powder this and throw it, in small portions at a time, into 200 parts of boiling distilled water, stirring constantly. Having added all of the mercuric sulphate, boil the mixture ten minutes, allow it to settle, decant the liquid, transfer the precipitate to a filter, wash it with hot distilled water until the washings cease to give an acid reaction on test-paper, and finally dry the product in a moderately warm place.

Reaction.— $\text{Hg} + 2\text{H}_2\text{SO}_4 + 2\text{HNO}_3 = 2\text{HgSO}_4 + 3\text{H}_2\text{O} + \text{N}_2\text{O}_5$. Then the mercuric sulphate is split up by water into a basic salt which precipitates, and an acid salt which remains in solution, the result varying somewhat according to the quantity of water used and its temperature.

Notes.—Mercuric sulphate can be made from mercury and sulphuric acid without the use of nitric acid; when the latter is added, however, the reaction is more easily accomplished.

Basic mercuric sulphate can also be made by gradually adding a solution of mercuric nitrate to a solution of sodium sulphate, the latter salt to be in excess.

Description.—A heavy lemon yellow powder, very slightly soluble in water, insoluble in alcohol or ether. When heated it turns red, but becomes yellow on cooling.

Tests.—It should dissolve in 20 parts of hydrochloric acid, showing absence of mercurous salt or lead. It should be completely volatile at high temperature.

THIOSULPHATES.

SODIUM THIOSULPHATE.

SODII HYPOSULPHIS.

[SODIUM HYPOSULPHITE.]



This important salt, better known by the old name of "hyposulphite of sodium," is prepared by boiling sulphur with solution of caustic soda, and passing sulphurous oxide into the liquid until colorless, or by boiling sulphur with solution of sodium sulphite.

On evaporation large crystals having the above composition are obtained. The salt is used in the laboratory as a reagent in quantitative analysis, and very largely in the arts.

SULPHITES.

All of very limited solubility in water. Used in medicine on account of the available sulphurous acid they contain.

SULPHUROUS ACID.**ACIDUM SULPHUROSUM.**

The "sulphurous acid" of the Pharmacopoeia of the United States is an aqueous solution, representing 4.50 per cent. of H_2SO_3 , corresponding to 3.50 per cent. of sulphurous oxide (SO_2).

It is prepared as follows:

Sulphuric acid	70 Gm.
Charcoal, in coarse powder	10 Gm.
Distilled water	350 Gm.
Sodium carbonate	5 Gm.

Put the acid and the charcoal in a flask of about 200 C.c. capacity. Connect the flask by means of bent glass tubing and perforated rubber stoppers with a wide mouthed bottle of about 100 C.c. capacity, to be used as a wash-bottle and for that purpose one-third filled with water. The wash-bottle is to be fitted with a rubber stopper having three perforations—one for the glass tube connecting it with the flask used as a generator, another for a safety tube, and the third for the glass tube connecting the wash-bottle with the receiver, which should consist of a bottle of about 500 C.c. capacity. The tube between the generator and the wash-bottle, and also the safety-tube, should reach nearly to the bottom of the wash-bottle; the tube connecting the wash-bottle with the receiver should end just below the stopper of the wash-bottle above the surface of the wash water, and should dip about three centimeters below the surface of the distilled water which is put into the receiver. Connect the receiver in the same manner with the second wide-mouthed bottle of 50 C. c. capacity containing the sodium carbonate dissolved in 20 C.c. of water. The joints between the pieces of glass tubing should be of soft rubber. Having made all the joints tight, apply heat to the flask by means of a sand-bath, and continue the heating until the evolution of gas has nearly ceased, keeping the receiver at or below 10°C . (50°F .) by means of cold water or crushed ice. Then remove the receiver, shake the contents, and keep the product in dark, amber colored, glass stoppered bottles, in a cool and dark place.

Reaction.— $4\text{H}_2\text{SO}_4 + 2\text{C} = 4\text{SO}_2 + 2\text{CO}_2 + 4\text{H}_2\text{O}$.

Notes.—As soon as the reaction ceases the wash-bottle must be at once disconnected from the generator; otherwise the vacuum produced in the latter will cause the liquid in the wash-bottle to be forced back into the flask, causing its fracture. The solution of sodium carbonate in the end-bottle is to absorb the gas which is not absorbed by the water in the receiver.

Description.—A colorless solution with strong characteristic odor of burning sulphur, and sharp acid taste and reaction. Its specific gravity is 1,022 to 1,023.

Tests.—It is completely volatile by heat, and should be free from sulphuric acid as shown by tests with BaCl_2 after adding hydrochloric acid. For quantitative valuation see method described later.

Saturating power.—100 parts of the official solution of sulphurous acid will neutralize:

Potassium carbonate, 9.3 parts.....	}	Yielding 10.6 parts of potassium sulphite.
Potassium bicarbonate, 11 parts....		
Sodium carbonate, 15.7 parts.....	}	Yielding 13.8 parts of sodium sulphite.
Sodium bicarbonate, 9.2 parts.....		
Calcium oxide, 3 parts.....	}	Yielding 8.5 parts of calcium sulphite.
Calcium hydrate, 4 parts.....		
Magnesia, 2.2 parts.....	}	Yielding 11.6 parts of magnesium sulphite.

POTASSIUM SULPHITE.

POTASSII SULPHIS.



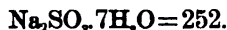
Prepared by passing sulphurous oxide into a solution of potassium carbonate until all carbonic acid has been expelled, and then adding another equal quantity of potassium carbonate. The solution is then evaporated to crystallization. See Sodium Sulphite.

Description.—Colorless crystals or powder, readily soluble in water, and but slightly in alcohol. Decomposed by acids yielding SO_2 without deposit of sulphur.

Tests.—For the quantitative valuation see the method given later.

SODIUM SULPHITE.

SODII SULPHIS.



Prepared by saturating a solution of sodium carbonate with sulphurous oxide, and then adding another equal quantity of sodium carbonate, after which the solution is evaporated to crystallization. The process

is analogous to that for making potassium sulphite. In both cases a bisulphite is first made, and this is converted into normal sulphite by the addition of a quantity of the alkali equal to the amount used in making the bisulphite.

Description.—Colorless prisms or powder, resembling potassium sulphite in most of its properties.

Tests.—The value of the salt can be determined by iodine solution, as described later.

CALCIUM SULPHITE.

CALCII SULPHIS.



By saturating milk of lime with sulphurous oxide, and collecting and drying the precipitate formed.

Description.—A white powder but slightly soluble in water, soluble in sulphurous acid. This solution is sometimes used to check fermentation. The salt gradually oxidizes to sulphate.

Tests.—The dry salt yields sulphurous oxide when heated with acids. Its value is determined by solution of iodine.

MAGNESIUM SULPHITE.

MAGNESII SULPHIS.



By saturating either magnesium carbonate or magnesium oxide, suspended in water, with sulphurous oxide, the crystalline product being drained and dried.

Description.—A white powder, easily soluble in water, insoluble in alcohol. It oxidizes in the air.

Tests.—Dissolves in hydrochloric acid with effervescence, but without producing a precipitate of sulphur. The solution tested with BaCl_2 should show only a slight turbidity at most.

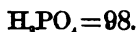
CHAPTER XVIII.

PHOSPHATES.

The phosphates of potassium, sodium and ammonium are water soluble; other phosphates, used in medicine and pharmacy, are insoluble in water. They are prepared by double decomposition.

PHOSPHORIC ACID.

ACIDUM PHOSPHORICUM.



Phosphoric acid can be made in various ways. It is most commonly made from phosphorus by oxidation with nitric acid. When strong nitric acid is used the reaction is more rapid and less heat is then applied; when the acid is diluted, the action being less violent, more heat is requisite.

It requires 16 parts of phosphorus to make 100 parts of the official phosphoric acid. The Pharmacopoeial formula is as follows:

Mix 500 Gm. of nitric acid with 500 C.c of distilled water in a tubulated retort capable of holding 2,000 C.c. Place the retort upon a sand-bath, or on a wire gauze support, connect it loosely with a well cooled receiver. Add 80 parts of phosphorus previously cut into very small pieces. Insert a funnel through the tubulus of the retort and then gradually apply heat until the reaction begins. Regulate the heat so as to prevent the action from becoming violent, checking it, if need be, by the addition of a little distilled water. Continue the digestion until all the phosphorus is dissolved, and return to the retort, from time to time, any liquid which may collect in the receiver.

When all the phosphorus is dissolved transfer the contents of the retort to a tared porcelain dish, and heat the liquid at a temperature of nearly but not above 190°C . (374°F .) until the excess of nitric acid is expelled and an odorless, syrupy liquid remains. Cool the dish and contents and add enough distilled water to make the total weight of the product 500 Gm.

Test the product for nitric, phosphorous and arsenic acids, all of which must be removed if present.

If nitric acid be present, evaporate the liquid until it ceases to give any further reaction for that acid; then let it cool and dilute it with distilled water until the prescribed weight (500 Gm.) is restored.

If phosphorous acid be found in the phosphoric acid, add 30 Gm. of nitric acid and again heat the mixture until reactions for phosphorous and nitric acids cease, and restore the prescribed weight (500 Gm.) by dilution with distilled water as in the case described.

Should arsenic be present, dilute the phosphoric acid with 750 C.c. of distilled water, heat the liquid to about 70°C . (158°F .) and then pass through it a stream of hydrogen sulphide gas for half an hour. Then remove the heat, but continue passing hydrogen sulphide through the dilute phosphoric acid until it becomes cold. Close the vessel tightly, set it aside for 24 hours, filter the liquid, then heat the filtrate until all odor of hydrogen sulphide has been expelled, filter again, and finally evaporate the now purified phosphoric acid until its weight is reduced to 500 Gm.

Preserve the product in glass stoppered bottles.

Reaction.—The principal reactions are, probably, first: $3\text{P}_4 + 6\text{HNO}_3 + 6\text{H}_2\text{O} = 6\text{H}_3\text{PO}_3 + 8\text{N}_2\text{O}_3$, and then $3\text{H}_3\text{PO}_3 + 2\text{HNO}_3 = 3\text{H}_3\text{PO}_4 + \text{N}_2\text{O}_2 + \text{H}_2\text{O}$.

Notes.—The phosphorus used must be free from sulphur; otherwise sulphuric acid will be formed from the latter and contaminate the product. This result might, however, be prevented by using an excess of phosphorus so that some of it remains undissolved, the phosphorous acid being oxidized to phosphoric acid by a fresh portion of nitric acid after removing the undissolved phosphorus and sulphur.

As the phosphorus fuses collecting on the bottom of the retort, or flask, where it presents but a limited surface of contact for the action of the nitric acid, the oxidation is slow. High heat renders the action too violent, unless the nitric acid has been properly diluted, as in the official process described above. Nitric acid of 1.20 sp. gr. is considered most suitable. Whenever the reaction is from any cause too violent, there is danger that particles of phosphorus may be thrown to the surface of the liquid and ignited, the heat from the combustion fracturing the vessel and scattering the burning phosphorus, the acid liquid, and the red nitrous fumes. The temperature need not exceed 50°C . (122°F .)

A flask can be used in place of the retort, and the heating can be done in a water-bath. In that case the neck of the flask should be covered by a watch crystal, the convex side downward, so that the liquid formed by the condensation of the rising vapors may run down into the flask again. Should the flask or retort break from any cause while undissolved phosphorus remains in it, the use of the water-bath instead of a sand-bath would prevent the ignition of the phosphorus.

Should the liquid, after the phosphorus has been dissolved, contain both phosphorous and arsenic acids, and should it then be concentrated to less than three times the weight of the phosphorus consumed, the phosphorous acid may be

oxidized by the concentrated nitric acid so violently that the liquid froths over the sides of the dish unless a little water is added. The arsenic then separates as a brown powder of reduced metal.

If the liquid contains phosphorous acid, but no nitric acid, the phosphorous acid may be lost during the subsequent evaporation, hydrogen phosphide being formed unless nitric acid be added to prevent it.



The expulsion of the excess of nitric acid may be known to have been accomplished when a piece of filter-paper dipped in ammonia water no longer gives off white fumes when held over the liquid.

All of the nitric acid must be expelled before the liquid is charged with hydrogen sulphide gas for the purpose of removing arsenic present. Otherwise sulphur deposits, which is afterwards oxidized into sulphuric acid.

To facilitate the removal of the nitric acid, Professor Lloyd employs a little purified alcohol, and Professor Markoe adds a small amount of pure oxalic acid.

The evaporation of the acid must be done in well glazed porcelain dishes to avoid contamination with silicic acid. When silicic acid is present in considerable quantity in concentrated phosphoric acid, it separates in gelatinous flocculi upon dilution after standing some time.

Other methods.—Phosphoric acid has also been made from phosphorus by the use of iodine or bromine and water. When bromine is employed the phosphorus combines with it, forming PBr_3 and PBr_5 ; the PBr_3 with $3\text{H}_2\text{O}$ yields $\text{H}_3\text{PO}_3 + 3\text{HBr}$, while the PBr_5 with $4\text{H}_2\text{O}$ yields $\text{H}_3\text{PO}_4 + 5\text{HBr}$; the H_3PO_3 with 2Br and H_2O will form $\text{H}_3\text{PO}_4 + 2\text{HBr}$. Thus ten molecules of HBr are formed simultaneously with two molecules of H_3PO_4 , these acids being separated by distillation and both utilized. Analogous reactions take place when iodine or chlorine is used instead of bromine. These processes are, however, dangerous on account of the violent chemical action and the explosive character of the compounds of phosphorus with the halogens.

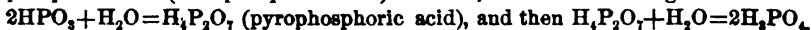
In other processes nitric acid is employed simultaneously with either bromine, or iodine, or both. The hydracid formed is then decomposed by the nitric acid liberating the halogen, which again acts upon a new portion of the phosphorus:



These processes are also dangerous. Markoe's method is probably the least dangerous of all of them. He mixes 576 parts of water, 96 parts of phosphorus, and 1 part of iodine in a stone jar placed in ice-water; then 4 parts of bromine dissolved in dilute hydrobromic acid are very cautiously added. After 24 hours the phosphorus is nearly or quite dissolved; if any of it remains undissolved after that period, heat may be safely applied to hasten its oxidation. The iodine, bromine and excess of nitric acid are then driven off by heat.

The slow oxidation of phosphorus by moist air at a low temperature has also been practiced.

Ortho-phosphoric acid has also been prepared by heating a solution of glacial phosphoric acid (metaphosphoric acid) in water, the reactions being:



A considerable quantity of pyrophosphoric acid may, however, remain undecomposed.

Amorphous phosphorus is readily oxidized by nitric acid without danger of fire.

The reaction begins after a few hours, generally without the application of any heat, and having once commenced it progresses very rapidly. If a capacious vessel is employed, no danger need be apprehended.

Properties.—An aqueous solution containing 50 per cent. of ortho-phosphoric acid and 50 per cent. of water. It is a clear, colorless liquid, without odor, of a strongly acid taste and reaction. Sp. gr. 1.347. Its sp. vol. is 0.742. When heated, the liquid loses water, and when a temperature of about 200°C . (392°F .) has been reached, the acid is gradually converted into pyrophosphoric and metaphosphoric acids, which may be volatilized at a red heat. If the diluted acid be superaturated with ammonia, addition of "magnesia mixture" produces a white, crystalline precipitate. If this precipitate be dissolved in diluted acetic acid, the solution yields a yellow precipitate with test solution of nitrate of silver.

Tests.—When the acid is mixed with water only, its value can be readily determined by means of the specific gravity of the solution. See the following table.

The amount of phosphoric acid in a solution can also be determined by means of the volumetric uranium solution as explained under the proper heading. Test for presence of arsenic by diluting largely with water and saturating with hydrogen sulphide gas.

The diluted acid treated with solution of barium chloride yields a white precipitate when sulphates are present. The diluted acid should not give a white precipitate of AgCl when treated with solution of silver nitrate.

When the acid is mixed with strong sulphuric acid and cooled, a crystal of ferrous sulphate added should not impart a brown color to the surrounding liquid, showing absence of nitric acid.

Specific Gravity and Percentage Strength of Solutions of H_3PO_4 .
(Schiff.)

Per cent. of H_3PO_4 .	Sp. gr. 15°.	Per cent. of H_3PO_4 .	Sp. gr. 15°.
1	1.0054	19	1.1130
2	1.0109	20	1.1196
3	1.0164	21	1.1262
4	1.0220	22	1.1329
5	1.0276	23	1.1397
6	1.0333	24	1.1465
7	1.0390	25	1.1534
8	1.0449	26	1.1604
9	1.0508	27	1.1674
10	1.0567	28	1.1745
11	1.0627	29	1.1817
12	1.0688	30	1.1889
13	1.0749	35	1.2262
14	1.0811	40	1.2651
15	1.0874	45	1.3059
16	1.0937	50	1.3486
17	1.1001	55	1.3931
18	1.1065	60	1.4395

Saturating power.—100 parts of the official (U. S.) phosphoric acid, containing 50 per cent. of orthophosphoric acid (H_3PO_4), will saturate:

Potassa, 57 parts.....	}	Yielding 88.8 parts of potassium phosphate.
Solution of potassa (5 per cent.), 1143 parts.....		
Potassium carbonate, 87 parts.....		
Potassium bicarbonate, 102 parts.....		
Soda, 41 parts.....	}	Yielding 182.6 parts of sodium phosphate.
Solution of soda (5 per cent.), 816 parts.....		
Sodium carbonate, 146 parts.....		
Sodium bicarbonate, 86 parts.....		
Ammonia (NH_3), 17.87 parts.....	}	Yielding 67.3 parts of ammonium phosphate.
Stronger water of ammonia (28 per cent.), 62 parts.....		
Water of ammonia (10 per cent.), 174 parts.....		
Ammonium carbonate, 53.4 parts.....		

Strength.—Table showing the strengths of the phosphoric acids of the Pharmacopœias:

Pharmacopœia.	Per cent. of H_3PO_4 .	Sp. gr. 15°C.	Number of parts representing 98 parts H_3PO_4 .
Great Britain	66.3	1.500	148
United States	50.	1.347	196
France.....	50.	1.347	196
Germany.....	20.	1.200	490

Composition.—Absolute ortho-phosphoric acid contains 8.061 per cent. of replaceable H, and the official acid, containing 50 per cent. of ortho-phosphoric acid, accordingly furnishes 48.469 per cent. of PO_4 .

Uses.—The utility of a stronger phosphoric acid than the diluted phosphoric acid of the Pharmacopœias was recognized in the sixth revision of the American Pharmacopœia. It is employed in making certain pharmaceutical preparations where a concentrated phosphoric acid is needed as a chemical solvent. It is also used for making diluted phosphoric acid.

DILUTED PHOSPHORIC ACID.

ACIDUM PHOSPHORICUM DILUTUM.

Phosphoric acid..... 1 part.
Distilled water..... 4 parts.
Mix.

Description.—An acid liquid whose density is 1.0567. Its sp. vol. is 0.946. Its general properties resemble those of the undiluted acid.

Tests.—This solution is examined for impurities and for percentage strength, as in the stronger acid.

Saturating power.—100 parts of the official (U. S.) diluted phosphoric acid, containing 10 per cent. of H_3PO_4 , will saturate:

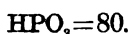
Potassa, 11.4 parts.....	}	Yielding 17.76 parts of potassium phosphate.
Solution of potassa (5 per cent.), 228.5 parts.....		
Potassium carbonate, 16.8 parts.....		
Potassium bicarbonate, 20.4 parts.....		
Soda, 8.16 parts.....	}	Yielding 36.5 parts of sodium phosphate.
Solution of soda (5 per cent.), 163.8 parts.....		
Sodium carbonate, 29.2 parts.....		
Sodium bicarbonate, 17.14 parts.....		
Ammonia (NH_3), 3.47 parts.....	}	Yielding 13.5 parts of ammonium phosphate.
Stronger water of ammonia (28% NH_3), 12.4 parts.....		
Water of ammonia (10% NH_3), 34.7 parts.....		
Ammonium carbonate, 10.7 parts.....		

Strength.—The following table shows the strengths of the diluted phosphoric acids of the various Pharmacopœias:

Pharmacopœia.	Per cent. of H_3PO_4 .	Sp. gr. 15°.	Number of parts representing 98 parts of H_3PO_4 .
Germany.....	20.	1.200	490
Great Britain.....	13.8	1.080	710
United States.....	10.	1.057	980

SYRUPY PHOSPHORIC ACID.

Under the name of syrupy phosphoric acid the manufacturing chemists sell a strong phosphoric acid of syrupy consistence. Different makers do not make it of the same strength; but the official concentrated phosphoric acid of the British Pharmacopœia (1885) represents a fair average strength. It is of 1.50 sp. gr., and contains 66.3 per cent. of H_3PO_4 .

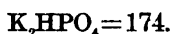
GLACIAL PHOSPHORIC ACID.**ACIDUM PHOSPHORICUM GLACIALE.**

This is meta-phosphoric acid, more or less contaminated with pyrophosphoric acid. As found in commerce it often also contains phosphates of sodium, calcium, magnesium, etc.

Description.—Commercially, a hard glassy mass, but softer and wax-like when pure. It is deliquescent, and dissolves readily in water and alcohol. The acid is volatile at a red heat.

Tests.—Gives white precipitates with solutions of barium chloride and white of egg.

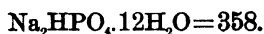
It can be converted, by boiling with water, into ordinary phosphoric acid, then tested for impurities as is this.

POTASSIUM PHOSPHATE.**POTASSII PHOSPHAS.**

Prepared in the same manner as sodium phosphate, using potassium carbonate to decompose the acid phosphate of calcium.

Potassium phosphate is a deliquescent, indistinctly crystalline, white mass, very freely soluble in water. At red heat it is converted into pyrophosphate of potassium, which is also deliquescent.

The tests for purity and per cent. of phosphoric acid are made as before.

SODIUM PHOSPHATE.**SODII PHOSPHAS.****[DI-SODIUM-HYDROGEN PHOSPHATE.]**

Bone-ash, in fine powder.	10 parts.
Sulphuric acid.	6 parts.
Sodium carbonate, sufficient.	

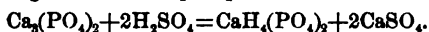
Wash the bone-ash with about ten times its weight of warm water. Then mix the washed mass with the sulphuric acid, stir well and set aside in a warm place for about three days, replacing the water which

may be lost by evaporation, and stirring occasionally. Then add 10 parts of boiling water, mix thoroughly, transfer the mixture to a muslin strainer, and let the liquid pass through. Reserve the liquid. Transfer the magma from the muslin to an earthenware vessel, add 10 parts of boiling water, stir well, and again strain the mixture through muslin, adding the colature to that previously reserved. Continue washing the residue with boiling water until the liquid passes nearly tasteless. Mix the several acid liquids and evaporate the mixture to 20 parts. Set this aside a few days. Filter. Heat the filtrate to the boiling point, and gradually add to it a solution of sodium carbonate in hot water, until a filtered portion of the now alkaline liquid effervesces when mixed with dilute sulphuric acid. Digest the mixture an hour or two, and then filter. Wash out the remaining sodium phosphate from the residue by means of hot water, adding the washings to the filtrate. Then evaporate the mixed liquids to 10 parts, and set aside to crystallize.

Purify the product by re-crystallization after dissolving it in twice its weight of water. Repeat the re-crystallization as many times as may be necessary to obtain a clean product.

Dry the crystals with as little exposure to the air as possible, to avoid efflorescence.

Reaction.—First the tri-calcium phosphate (bone-ash) is decomposed by the sulphuric acid yielding acid calcium phosphate and calcium sulphate as follows :



Then the acid phosphate of calcium is decomposed by the sodium carbonate as follows :



Notes.—When the bone-ash is treated with sulphuric acid the mixture becomes hot. Usually the powdered bone-ash is not washed previous to mixing it with the sulphuric acid, and no water added until after the powder and acid have first been thoroughly mixed. If organic matter be present in the bone-ash, sulphurous oxide is given off. Some carbon dioxide will also be given off from calcium carbonate in the bone-ash, and sometimes pyrosulphuric acid gas is formed at the same time. If the bone-ash is washed with water, the object of which is the removal of alkalies, the wash-water should be drained off thoroughly before mixing the moist mass with the acid. When the process is carried out on a small scale the washed and drained bone-ash, still wet, should be put in a tared vessel, the sulphuric acid mixed with it, and finally enough boiling water added to make the whole mixture weigh three times as much as the bone-ash used. After the mass has been digested a sufficient time to insure thorough decomposition of the basic calcium phosphate, to facilitate which the mass should be frequently and thoroughly stirred, the next step is the separation of the liquid containing the acid phosphate of calcium, with which the sodium phosphate is to be made, from the white mass of calcium sulphate which is to be thrown away after the acid liquid has been completely washed out from it and collected.

On a manufacturing scale this leaching process may be conveniently carried out in tubs provided with loose perforated diaphragms resting on suitable supports about four or five inches above their bottoms. A common whisky barrel sawed in two in the middle, furnishes two good tubs. A hole is bored in one side of each tub, about two inches above the bottom, and a tube about six inches in length is fitted tightly in the hole. A piece of very coarse, loose gunny-bagging is washed in warm water and, while still wet, spread out over the perforated false bottom so as to cover it and extend two or three inches up on the sides of the

tub all around. The mixture of bone-ash, acid and water is now put into the tub, which should be about half filled. A stick of wood four feet long furnishes a good stirrer. Boiling water is now poured upon the mass and well mixed with it, after which the liquid is allowed to percolate through the mass, and through the strainer, into the space between the perforated diaphragm and the bottom of the tub, and to run out through the tube into a bucket, or other suitable vessel.

When the liquor which passes from the tub is nearly tasteless, or no longer acid, the leaching is completed, the residue of calcium sulphate is thrown away, and the acid liquor is boiled down to twice the weight of the bone-ash used.

The concentrated solution of acid calcium phosphate is now allowed to stand a few days in order that the calcium sulphate held in solution may be deposited. It is then filtered, diluted with an equal volume of water, and heated to the boiling point. To the hot liquid is now added hot sodium carbonate solution as described.

The quantity of sodium carbonate required will depend upon the completeness of the decomposition of the bone-ash and the lixiviation—in other words, upon the amount of acid calcium phosphate contained in the liquor. If the work has been well done, it will require about 100 parts or more of sodium carbonate to render alkaline the acid liquor from 100 parts of bone-ash.

Hot liquids are employed in order that the calcium carbonate formed may be heavy, so as to separate as rapidly as possible. The sodium carbonate must be added gradually, because of the effervescence caused by the escaping carbonic oxide. Litmus paper cannot be used to ascertain when sufficient sodium carbonate has been added, because sodium phosphate itself has an alkaline reaction. After the further addition of sodium carbonate has ceased to cause effervescence, it is necessary to remove a small portion of the liquid, filter it, and test it by pouring it into a small amount of dilute sulphuric acid, when it should effervesce. The slight excess of sodium carbonate added is necessary to insure satisfactory crystallization of the sodium phosphate, and the carbonate remains in the mother liquor.

When the liquid contains an excess of sodium carbonate, the precipitated calcium carbonate is filtered out and washed on the filter with a little hot water, the washings being added to the previous filtrate. Evaporate the filtrate until reduced to about three times the weight of the sodium carbonate consumed, or until a pellicle begins to form on the surface. Then set it aside to crystallize.

The crystallization is best effected when an excess of sodium carbonate is present and the solution is not too concentrated. It should not be hastened by evaporating down the solution too far, because the salt then crystallizes with only 7 instead of 12 molecules of water of crystallization.

The product generally requires purification by recrystallization to obtain a sodium phosphate which answers the description and tests of the Pharmacopœia.

Description.—Colorless transparent crystals, having a specific gravity of 1.55. They effloresce readily, and when slightly heated melt in their water of crystallization. The solubility of the salt increases rapidly with the temperature. Insoluble in alcohol.

Tests.—The solution has a slight alkaline reaction. It should not effervesce on addition of acids (from presence of carbonate). The solution acidified with hydrochloric acid should not yield a white precipitate when treated with barium chloride, nor should it yield a precipitate or color with hydrogen sulphide.

The amount of phosphoric acid present in a solution of sodium phosphate can be determined by means of standard uranium solution.

DRIED SODIUM PHOSPHATE.

SODII PHOSPHAS EXSICCATUS.



When heated to 35° C. (95° F.) sodium phosphate begins to dissolve in its water of crystallization, but does not liquefy perfectly until at about 40° C. (104° F.). If allowed to cool again it solidifies into a

mass having a radiated crystalline texture. When heated above 40°C . the salt loses 5 molecules of water. At 100°C . (212°F .) all the water of crystallization is expelled and "dried phosphate of sodium" remains. This product should not be confounded with the "effloresced sodium phosphate," which is the white powder formed by the gradual efflorescence of sodium phosphate in dry warm air, and which contains 47 per cent. of water = $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$.

Dried sodium phosphate may be made by heating crystallized sodium phosphate over a water-bath until it ceases to lose weight, stirring the mass when it becomes dry, and finally heating it over a sand-bath to about 120°C . (248°F .).

The product gradually absorbs moisture from the air until converted into $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$.

It must be kept in tightly corked bottles. It is a white powder, entirely soluble in water, and its solution answers to the tests for sodium phosphate.

SODIUM AND AMMONIUM PHOSPHATE.

SODII ET AMMONII PHOSPHAS.

[MICROCOSMIC SALT.]



Sodium phosphate 5 parts.

Ammonium phosphate 2 parts.

Dissolve the salts in 20 parts of hot water, add a little ammonia so as to render the liquid alkaline to turmeric paper, filter, and set aside to crystallize.

The crystals effloresce; their solution has a slight alkaline reaction.

The salt is used as a reagent in blow-pipe analysis.

AMMONIUM PHOSPHATE.

AMMONII PHOSPHAS.



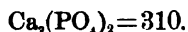
Prepared in the same manner as sodium phosphate, using ammonium carbonate instead of sodium carbonate to neutralize the acid liquor. Ammonia being volatile and hence driven off in the evaporation to crystallization, ammonia water must be added from time to time in just sufficient quantity to keep it in slight excess.

The crystals are readily soluble in water, but not in alcohol. The water solution may be tested for impurities, as is sodium phosphate.

TRI-CALCIUM PHOSPHATE.

CALCII PHOSPHAS PRÆCIPITATUS.

[PRECIPITATED PHOSPHATE OF CALCIUM.]



Bone-ash is obtained by the calcination of bones. It is the inorganic residue left on burning bones to whiteness, and consists mainly of tri-calcium phosphate with about ten per cent. of calcium carbonate and a little calcium fluoride and magnesium phosphate. It is used in the manufacture of glacial phosphoric acid, precipitated calcium phosphate, sodium phosphate, etc.

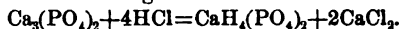
It should be white or but slightly grayish, odorless, and almost completely soluble, with but slight effervescence, in dilute hydrochloric acid.

Precipitated tri-calcium phosphate is prepared as follows:

Bone-ash, in fine powder	300 Gm.
Hydrochloric acid	450 C.c.
Ammonia water, sufficient.	

Digest the bone-ash with the acid, diluted with 1,500 C.c. of water, until dissolved. Boil the solution a few minutes; filter; then add 1,500 C.c. of boiling water. Now add ammonia water until the mixture acquires an alkaline reaction. Collect the precipitate on a muslin strainer, wash it with boiling water until the washings cease to produce a precipitate with test solution of silver nitrate acidulated with nitric acid. Dry the washed precipitate at a temperature not exceeding 100° C. (212° F.).

Reaction.—When the crude tri-calcium phosphate is dissolved in hydrochloric acid, the reaction occurring is as follows:



When ammonia is added to the solution both the acid calcium phosphate and the calcium chloride are decomposed, $\text{CaH}_4(\text{PO}_4)_2 + 2\text{CaCl}_2 + 4\text{NH}_4\text{OH} = 4\text{NH}_4\text{Cl} + 4\text{H}_2\text{O} + \text{Ca}_3(\text{PO}_4)_2$.

Notes.—Hot liquids are employed for the precipitation in order that the product may be dense and easily washed. If the precipitation be effected in cold water the precipitated calcium phosphate is very voluminous, light, presenting a gelatinous appearance, and the washing becomes difficult.

By-product.—The ammonium chloride should be recovered from the mother liquor after the precipitation, and purified.

Description.—This product differs from the bone-ash, chiefly in its greater purity. It still contains small traces of calcium fluoride and magnesium phosphate.

SYRUP OF LACTOPHOSPHATE OF CALCIUM.**SYRUPUS CALCH LACTOPHOSPHATIS.**

Precipitated calcium carbonate.....	4 Gm.
Lactic acid	10 Gm.
Phosphoric acid (50%)	5 Gm.
Orange-flower water.....	25 C.c.
Sugar.	200 Gm.
Distilled water, sufficient.	

Mix the lactic acid with 30 C.c. of distilled water, and gradually add the calcium carbonate, warming gently if necessary, to dissolve the carbonate. Then add the phosphoric acid, previously diluted with 30 C.c. of distilled water. Next add the orange-flower water. Filter the liquid, and pass enough distilled water through the filter to make the total filtrate measure 130 C.c. In this dissolve the sugar without the aid of heat.

Note.—This syrup is of the same strength as that of the official preparation, and keeps better.

(Formula of R. Rother, modified by Geo. T. Williams.—*Am. J. Ph.*)

FERRICO-FERROUS PHOSPHATE.**FERRI PHOSPHAS COERULEUS.**

[**Blue Phosphate of Iron.**—The "Phosphate of Iron" of the British Pharmacopœia and the United States Pharmacopœia of 1870.]

Ferrous sulphate	30 parts.
Sodium phosphate.....	28 parts.
Sodium bicarbonate.....	7 parts.

Dissolve the ferrous sulphate and the sodium phosphate each in 300 parts of boiling water, filter, and allow the solutions to cool to about 40° to 50° C. (104° to 122° F.). Dissolve the sodium bicarbonate in 50 parts of water. Add the solution of ferrous sulphate to the solution of sodium phosphate, and lastly add the solution of sodium bicarbonate. Mix well. As soon as the precipitate has subsided, decant the mother liquor. Wash the precipitate, either by decantation or on a muslin strainer, with hot water, until the washings cease to give a precipitate with solution of barium chloride. Dry the product at not over 50° C. (122° F.).

Reaction.— $3\text{FeSO}_4 + 2\text{Na}_2\text{PHO}_4 = \text{Fe}_3(\text{PO}_4)_2 + 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$. The sulphuric acid is then neutralized by sodium bicarbonate, and the precipitated ferrous phosphate is partially oxidized.

Notes.—Unless sodium bicarbonate, sodium acetate, or sodium phosphate in excess be added, a portion of the ferrosiferrous phosphate remains in solution in the free acid formed by the first reaction, and loss ensues. By neutralizing the free sulphuric acid with sodium bicarbonate, which does not affect the precipitate already formed, all of the phosphate of iron is thrown down. When first formed the precipitate is grayish white or bluish gray; it soon becomes grayish blue, and should retain this color until washed and dried. The color may be easily spoiled, however, by too high heat, or by too long exposure to the action of the mother liquor, or to the air during the process of washing and drying. Instead of bluish the color may become greenish gray. After drying, the product must be powdered and sifted. Dried at a high heat, the preparation forms very hard lumps; but if dried by moderate heat it may be easily rubbed through a fine sieve without using much force.

Description.—The salt should be entirely insoluble in water, and the solution in hydrochloric acid should yield no tests for copper, arsenic or other metals.

SYRUP OF PHOSPHATE OF IRON.

SYRUPUS FERRI PHOSPHATIS; B.

Precipitated ferrous sulphate.....	28 Gm.
Sodium phosphate	25 Gm.
Sodium bicarbonate	7 Gm.
Phosphoric acid (50%).....	136 Gm.
Sugar.....	450 Gm.

Dissolve the ferrous sulphate in about 300 C.c. of boiling water, and the sodium phosphate in a similar quantity of cold water; mix the solutions; add the sodium carbonate previously dissolved in 100 C.c. of water, and, after stirring well, transfer the precipitate to a muslin filter and wash it with distilled water until the filtrate ceases to be affected by test solution of barium chloride. Mix the washed and drained precipitate in a mortar with the phosphoric acid. As soon as the phosphate is dissolved, filter the solution into a bottle, add 400 C.c. of distilled water and the sugar, and shake until dissolved, without the aid of heat. Lastly, add sufficient distilled water to make the final product measure 660 C.c.

Notes.—The product contains about 1 Gm. of anhydrous phosphate of iron ($\text{Fe}_3(\text{PO}_4)_2$) in one imperial fluidrachm. If the quantity obtained by the above formula be diluted with 80 C.c. of simple syrup, the preparation will then contain 1 Gm. to each U. S. fluidrachm.

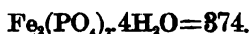
Practically the same product is obtained by the following method taken from Martindale's "Extra Pharmacopœia:"

Iron wire, polished, cut.....	7 Gm.
Phosphoric acid (50 %).....	120 Gm.
Distilled water	40 C.c.
Simple syrup.....	600 C.c.

Put the iron wire, acid, and water into a flask, being careful that the metal is completely covered by the liquid; insert a loose plug of cotton in the neck of the flask, and set it aside for two or three days. When the iron is dissolved, filter the liquid, add the syrup, and lastly enough distilled water to make the final product measure 820 C.c.

PRECIPITATED FERRIC PHOSPHATE.

FERRI PHOSPHAS PRÆCIPITATUS ALBUS.



Solution of normal ferric sulphate.....	660 C.c.
Sodium phosphate.....	450 Gm.
Sodium acetate.....	170 Gm.

Dilute the solution of ferric sulphate with 4,000 C.c. of water; add the sodium acetate, and dissolve. Dissolve the sodium phosphate in 4,000 C.c. of water, and filter, if necessary. Pour the solution of ferric sulphate and sodium acetate gradually into that of the sodium phosphate, stirring well. Wash the precipitate with warm water until the washings are free from sulphate. Collect and dry the precipitate with the aid of gentle heat.

Reaction. — $\text{Fe}_2(\text{SO}_4)_3 + 2(\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}) + 2(\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}) + 4\text{H}_2\text{O} = \text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} + 8(\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}) + 2\text{HC}_2\text{H}_3\text{O}_2$.

Notes.—It will be seen from the equation that the sodium acetate is added simply to prevent the formation of free sulphuric acid, which would occasion loss of ferric phosphate, which is soluble in that acid but insoluble in acetic acid.

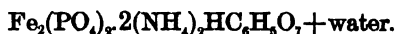
The precipitate is white or cream-colored and very voluminous. On this account it is difficult to wash. When the quantity operated upon admits of it, the washing should be effected by mixing the precipitate with warm water in a tall vessel, allowing it to settle, drawing off the clear supernatant liquid by means of a siphon, and then transferring the magma to a wetted muslin strainer where it may be left to drain thoroughly. This operation may be repeated if necessary.

When the precipitate is allowed to remain long in contact with the mother liquor it gradually becomes more dense; also when the washing is too long continued. If large quantities are operated upon the process consumes about a week.

Lac Ferri, or "milk of iron," is water in which freshly precipitated and washed ferric phosphate is held in suspension; the preparation contains from 1 to 1.20 per cent. of the phosphate.

AMMONIO-FERRIC CITRO-PHOSPHATE.

SOLUBLE PHOSPHATE OF IRON WITH CITRATE OF AMMONIUM.



Add the washed precipitated ferric phosphate obtained by the formula given above from 66 C.c. of solution of normal ferric sulphate and 45 Gm. of sodium phosphate, to 60 C.c. of di-ammonium hydrogen

citrate prepared by the formula given later under the head of Citrates. Heat the mixture by means of a water-bath for three hours, stirring occasionally, taking care not to allow the temperature to exceed 60° C. (140° F.). Evaporate the solution to the consistence of thick syrup, spread it on plates of glass, and dry it in scales.

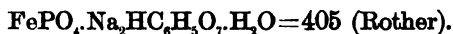
Notes.—The ferric phosphate is added in slight excess in order to perfectly saturate the solution with it.

If 60 C.c. of solution of di-sodium-hydrogen citrate be used instead of the citrate of ammonium, the product will be the Pharmacopœial soluble "phosphate of iron" (1880).

SODIO-FERRIC CITRO-PHOSPHATE.

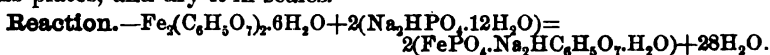
FERRI PHOSPHAS SOLUBILIS.

[PHOSPHATE OF IRON; U. S. P., 1880.]



Ferric citrate 5 parts.
Sodium phosphate..... 6 parts.

Dissolve the citrate in 18 parts of distilled water heated over a water-bath. Add the phosphate, and stir the mixture, continuing the heat until the color changes to green. Evaporate the solution at not over 60° C. (140° F.) to the consistence of thick syrup, spread it on glass plates, and dry it in scales.

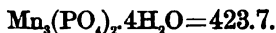


Notes.—Ferric phosphate is soluble in a solution of sodium citrate, forming a double salt which is very soluble in water, and forms scales when the concentrated solution is dried on plates. See Soluble Ferric Pyrophosphate.

Description.—Thin green scales, which grow dark in the light. Readily soluble in water, insoluble in alcohol.

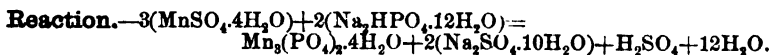
MANGANOUS PHOSPHATE.

MANGANI PHOSPHAS.



Manganous sulphate..... 10 parts.
Sodium phosphate..... 11 parts.

Dissolve the salts, separately, each in 80 parts of hot water, filter, and let the solutions cool. Mix them. Wash the precipitate with water until the washings cease to give any reaction for sulphate. Dry the product with the aid of gentle heat, avoiding unnecessary exposure to the air.



Notes.—As will be seen, the reaction is analogous to that occurring in the preparation of ferroso-ferric phosphate. Loss of product is sustained by reason of the solubility of manganous phosphate in the sulphuric acid formed. The free acid may be carefully neutralized by the addition of sodium bicarbonate to obviate this loss.

Description.—Whitish crystalline powder, soluble in hydrochloric acid. The solution in water is not very stable, especially in contact with air.

PYROPHOSPHATES.

SODIUM PYROPHOSPHATE.

SODII PYROPHOSPHAS.



Prepared by heating sodium phosphate in a porcelain or iron dish, raising the heat gradually until the salt fuses in its water of crystallization, then falls to powder as that water is expelled, and finally decomposes at a temperature of 240° to 300° C. (464° to 572° F.), being converted into normal sodium pyrophosphate. The dry powder is dissolved in a sufficient quantity of boiling water—about five times its weight—the solution is filtered while hot, and then set aside to crystallize. More crystals are to be obtained from the mother liquor upon evaporation.



Notes.—Sodium phosphate, in solution, yields a yellow precipitate with test-solution of silver nitrate acidulated with nitric acid; sodium pyrophosphate yields a perfectly white precipitate with the same reagent. The conversion of the phosphate is, therefore, known to be completed when a sample of the dry powder, dissolved in water, yields a white precipitate with silver nitrate.

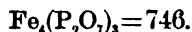
From 716 parts of sodium phosphate, the yield of pyrophosphate of sodium should be 446 parts, or nearly 62 per cent.

Description.—Clear prisms, readily soluble in water, insoluble in alcohol. It fuses to a glass at a red heat. When in solution it is converted into ortho-phosphate by boiling with acids.

Tests.—When the solution of the salt in water is acidified with hydrochloric acid effervescence should not occur. This solution should give no precipitate with hydrogen sulphide or with barium chloride.

PRECIPITATED FERRIC PYROPHOSPHATE.

FERRI PYROPHOSPHAS PRÆCIPITATUS.



Solution of normal ferric sulphate	500 C.c.
Sodium pyrophosphate	320 Gm.

Dilute the solution of ferric sulphate with 3,500 C.c. of water, and dissolve the pyrophosphate of sodium in 4,000 C.c. of hot water. Filter the liquids. Pour the solution of ferric sulphate slowly into that of the pyrophosphate, stirring well. Wash the precipitate with warm water on a wetted muslin strainer until the washings are free from sulphate. Dry the product by the aid of gentle heat.



Notes.—The solutions must be cold when mixed, and the iron solution must be added very slowly to that of the sodium salt, with constant and brisk stirring. The precipitate is very light and bulky, and hence quite difficult to wash.

Description.—A salt insoluble in water, but soluble in solutions of citrates, yielding double salts.

SOLUBLE FERRIC PYROPHOSPHATE.

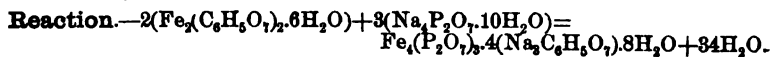
FERRI PYROPHOSPHAS; U. S. P.

[SODIO-FERRIC CITRO-PYROPHOSPHATE.]



Ferric citrate 9 parts.
Sodium pyrophosphate 10 parts.

Dissolve the citrate in 36 parts of distilled water heated on a water-bath, add the pyrophosphate, and continue the heating with constant stirring until the pyrophosphate of sodium is dissolved and the solution turns green. Evaporate at a temperature not exceeding 60° C. (140° F.) until the solution has the consistence of thick syrup; spread it on glass plates, and dry it in scales.

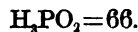


Notes.—Sodium citrate has been substituted for ammonium citrate for the preparation of pyrophosphate of iron by the last revision of the Pharmacopœia, on the ground that the ammonio-ferric salt became insoluble through loss of ammonia, and because it either darkened or became opaque by age. The sodio-ferric pyrophosphate, however, is also liable to become impaired by age and exposure to light. The preparation is difficult to scale satisfactorily. In small quantities it may be best scaled in the cold. Pyrophosphate of iron should be carefully protected against light. It is best preserved in amber colored bottles, tightly corked, and kept in a dry, cool, dark place.

Soluble ferric pyrophosphate with ammonium citrate may be prepared by adding the precipitated ferric pyrophosphate obtained from 500 C.c. of solution of normal ferric sulphate and 320 Gm. of sodium pyrophosphate according to the formula given on page 223, to 460 C.c. of the solution of di-ammonium hydrogen citrate prepared as described later, and digesting at not over 60° C. (140° F.) for three hours, or until no more of the ferric pyrophosphate dissolves. The solution is then filtered, evaporated, and the preparation scaled.

HYPOPHOSPHITES.

The hypophosphites of potassium, sodium, calcium and iron are used. The first three are water soluble; ferric hypophosphite is not insoluble, but nearly so. The calcium hypophosphite, which is prepared by boiling phosphorus with milk of lime, is used for making the hypophosphites of potassium and sodium by double decomposition with the carbonates.

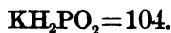
HYPOPHOSPHOROUS ACID.**ACIDUM HYPOPHOSPHOROSUM.**

Prepared by decomposing calcium hypophosphite with oxalic acid:

Calcium hypophosphite	48 parts.
Oxalic acid	35 parts.

Dissolve the hypophosphite in 300 parts of water, and add the oxalic acid previously dissolved in 150 parts of water, stirring well. Filter off the calcium oxalate, and evaporate the filtrate to 375 parts.

The product is a solution containing 10 per cent of H_3PO_2 .

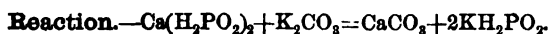
POTASSIUM HYPOPHOSPHITE.**POTASSII HYPOPHOSPHIS.**

Calcium hypophosphite	1 part.
Potassium carbonate	1 part.

Dissolve each salt separately in 7 parts of boiling water. Mix the solutions. Filter off the calcium carbonate, and evaporate the filtrate to dryness, over a water-bath, stirring constantly so as to obtain a granular product.

Notes.—The temperature during the evaporation should not exceed 85°C . (185°F .), as hypophosphites are prone to decompose with violent explosion when heated to nearly 100°C ., or higher.

The product may be freed from potassium carbonate and other impurities by dissolving it in ten times its weight of alcohol, filtering, evaporating the solution to the consistence of thick syrup, and setting this aside to solidify into a crystalline mass.



Description.—A white granular salt, easily soluble in water and weak alcohol. It may be obtained in crystalline form from the aqueous solution.

It is a strong reducing agent, and in presence of acids is capable of reducing salts to condition of lower oxide or metal. The solution should not effervesce with acids, and when treated with the proper reagents should give no tests for sulphates or phosphates, nor for calcium or magnesium.

SODIUM HYPOPHOSPHITE.

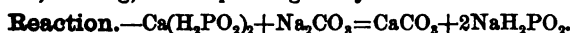
SODII HYPOPHOSPHIS.



Calcium hypophosphite 6 parts.
Sodium carbonate 10 parts.

Dissolve each salt in 60 parts of boiling water, and mix the solutions. Filter out the calcium carbonate, and evaporate the solution over a water-bath until a dry granular salt remains, taking care that the temperature during the evaporation does not exceed 85°C . (185°F .).

Notes.—May be purified by re-dissolving it in ten times its weight of hot alcohol, filtering, and evaporating to dryness.



Description.—Resembles closely the corresponding salt of potassium. The dry granular salt is deliquescent.

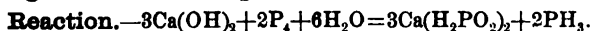
Tests.—The ordinary tests should show absence of carbonates, sulphates and phosphates, and of calcium.

CALCIUM HYPOPHOSPHITE.

CALCII HYPOPHOSPHIS.



Prepared by adding 1 part of granulated phosphorus to a milk of lime prepared from 4 parts of calcium oxide and 40 parts of water, exposing the mixture to the air at a temperature of 55°C . (131°F .), or even at the ordinary temperatures, stirring frequently, until all of the phosphorus has dissolved. The solution is filtered, carbonic acid gas passed through it to precipitate the lime held in solution as calcium hydrate; then the liquid is filtered again, and evaporated over a water-bath to dryness with constant stirring, to obtain a granular product, taking care that the temperature does not rise above 85°C . (185°F .).



Notes.—When phosphorus is digested with alkalis—whether potassium, sodium or calcium hydrate—the products are mainly hypophosphites and hydrogen phosphide. The hydrogen phosphide is an inflammable gas, having a strong garlic odor. Phosphates and free hydrogen are also formed when the conditions are favorable. At lower temperature much less hydrogen phosphide is formed than when the mixture is boiled. When boiling heat is employed the process is dangerous, explosions having frequently resulted when solutions of hypophosphites have been heated at or near the boiling point.

Description.—A white salt which is permanent in the air, but which oxidizes in water, in which it is readily soluble. Like other hypophosphites it is a strong reducing agent.

Tests.—The salt should be completely soluble in water, and the solution should not effervesce with acids. Barium chloride should not produce turbidity in the acidified solution.

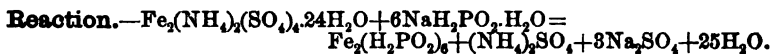
FERRIC HYPOPHOSPHITE.

FERRI HYPOPHOSPHIS.



Sulphate of iron and ammonium 30 parts.
Sodium hypophosphite 20 parts.

Dissolve each salt in 150 parts of water, and filter the solutions. Add the solution of the iron alum to that of the sodium hypophosphite, stirring constantly. Set aside for a few hours. Transfer the precipitate to a wetted filter or muslin strainer, drain it thoroughly, and wash it with 150 parts of cold distilled water. Drain, press out as much as possible of the moisture from the magma, and dry the product between blotting paper with the aid of gentle heat, protecting the preparation as far as practicable from the air.



Notes.—The quantity of water used is necessarily limited to prevent loss, because ferric hypophosphite is not quite insoluble in water, and if the washing should be done with the large quantities of water required to thoroughly remove the sulphates of the mother liquor from the bulky magma of hypophosphite, considerable loss must follow, if not the disappearance of the entire product. The precipitate must, therefore, be carefully freed from all mother liquor that can be removed by draining it before it is washed, and the quantity of water prescribed for washing it should not be exceeded.

Ferric hypophosphite is soluble in a strong solution of alkaline citrates, and a “scale salt” can be made by saturating solution of ammonium citrate with the freshly precipitated and washed magma, filtering the liquid, evaporating to the consistence of syrup, and spreading it on plates to dry.

Description.—A grayish powder slightly soluble in water, readily soluble in acetic acid, and in solutions of alkaline citrates.

CHAPTER XIX.

CARBONATES.

The alkali carbonates are all water soluble; those of barium, calcium and magnesium are insoluble, as are also the carbonates of the heavy metals. All the insoluble carbonates are prepared by precipitation.

CARBON DIOXIDE.

ACIDUM CARBONICUM.

[CARBONIC ACID.]

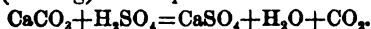
 $\text{CO}_2 = 44.$

Put into a flask a convenient quantity of marble, in small pieces, and add enough distilled water to cover it. Connect this generator by means of the required fittings with a wash-bottle containing distilled water, and provide the wash-bottle with a bent glass tube for conducting the gas wherever it may be necessary. Add hydrochloric acid gradually, through a safety tube, to the marble and water.

Reaction.— $\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2.$

Notes.—When calcium carbonate, either in form of marble or chalk, is used for generating carbonic acid gas by double decomposition with hydrochloric acid, the by-product of calcium chloride may be recovered, or its solution may be used for the preparation of precipitated calcium carbonate.

When sulphuric acid is employed instead of HCl, calcium sulphate is formed. Chalk and sulphuric acid are not readily mixed for making carbonic acid in the manufacture of mineral waters on a large scale, owing to the fact that the whiting used contains enough moisture to render it lumpy, so that a portion of it is not acted upon by the acid. Chalk, moreover, contains animal and bituminous matters, and, therefore, yields an impure carbonic acid gas of disagreeable odor and taste, which are with great difficulty removed. Chalk is nevertheless very generally employed, and sulphuric acid is used in preference to hydrochloric acid, because the latter is not only dearer but requires a larger acid chamber. The reaction, when chalk (whiting) and sulphuric acid are the materials used, is:



The prompt removal of the calcium sulphate from the generator as soon as the chalk has been consumed, is necessary, in view of the fact that a hard mass is soon formed by the residue, which will be found troublesome to remove.

Assuming that the chalk used contains 90 per cent. of CaCO_3 , and the sulphuric acid 92 per cent. of H_2SO_4 , it will require 10,000 parts of chalk and 9,600 parts of acid to produce 8,960 parts of CO_2 . At 20°C . (68°F .) 8,960 Gm. of carbonic acid gas measures 2,200 liters.

Sodium bicarbonate furnishes a purer carbonic acid gas than can be obtained from chalk.

Several experiments, showing properties of CO_2 , have already been given.

POTASSIUM CARBONATE.

POTASSII CARBONAS.

[POTASH. PEARL-ASH. SALTS OF TARTAR.]



Potassium carbonate is contained in wood ashes, and may be washed out of the ashes by lixiviation, the salt being recovered from the solution by boiling it down to dryness. The residue is then purified by heating it strongly in a furnace until all organic matters have been destroyed. Calcined potash is the result; it contains 50 to 80 per cent. of potassium carbonate, and is contaminated with sulphate, chloride, etc. By converting this crude potassium carbonate into bicarbonate, most of the impurities are removed, and a nearly pure normal carbonate can then be prepared from the bicarbonate.

Formerly, pure potassium carbonate was prepared by strongly heating (detonating) potassium bitartrate with half its weight of potassium nitrate.

At Stassfurth, potassium carbonate is prepared as follows: A solution of magnesium sulphate (*kieserite*) is mixed with a solution of crude potassium chloride, both of the materials being taken from the Stassfurth mines; a double salt of sulphate of potassium and magnesium is then formed together with a double chloride (*carnallite*): $3\text{KCl} + 2\text{MgSO}_4 = \text{K}_2\text{Mg}(\text{SO}_4)_2 + \text{KMgCl}_2$. The double sulphate is boiled with more potassium chloride, which results in the formation of potassium sulphate and carnallite. The carnallite decomposes slowly in water so that the magnesium chloride can be separated, and the potassium chloride is then used over again as before— $\text{K}_2\text{Mg}(\text{SO}_4)_2 + 3\text{KCl} = 2\text{K}_2\text{SO}_4 + \text{KMgCl}_2$. The potassium sulphate is then turned into carbonate by a process analogous to Leblanc's method for manufacturing soda. (See later.) The resulting product contains 92 to 93 per cent. of potassium carbonate, 2 or 3 per cent. of sodium carbonate, 2 per cent. of potassium chloride, and 1 to 2 per cent. of potassium sulphate.

Crude potash may be partly purified by dissolving it in twice its weight of water, letting it stand two days, decanting, filtering through linen, and evaporating the clear liquid in a clean iron vessel until a pellicle begins to form on the surface. The liquid is then put in a stone pot and set aside for a week, in order that sulphates, chlorides, etc., may crystallize out. The solution is then filtered and boiled down to dryness in an iron pot, stirring constantly at the close so as to obtain a dry, granular product.

Pure potassium carbonate for pharmaceutical and medicinal uses is most readily obtained by heating potassium bicarbonate until the residue is entirely soluble in twice its weight of water.

Being very deliquescent, potassium carbonate must be kept in tightly closed vessels.

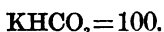
Description.—A white salt, sometimes crystalline, but generally as a granular powder, very soluble in water but not in alcohol. It dissolves with effervescence in acids, even when quite dilute.

Tests.—It should form a clear solution with water. This solution should not become turbid when treated with ammonium sulphide or carbonate. The solution in nitric acid should not show more than a slight turbidity when treated with silver nitrate or barium nitrate. When dried and heated to redness the salt should not lose more than 18 per cent. in weight.

By dissolving the weighed salt in dilute hydrochloric acid in excess, evaporating carefully to dryness and weighing again, this last weight should be to the weight of the carbonate as 1 to .928.

POTASSIUM BICARBONATE.

POTASSII BICARBONAS.



Prepared by treating potassium carbonate with carbonic acid gas. The gas is either conducted into a concentrated solution of the carbonate, or over the moist salt. To facilitate the absorption of carbonic acid the potash is mixed with powdered charcoal. The moist mass is exposed to the action of the carbonic acid gas until a test portion in solution no longer precipitates a solution of magnesium sulphate.

The black mass is mixed with water, heated to about 70° or 80° C. (158° to 176° F.), the solution is filtered while warm to remove the charcoal and the silica which has been precipitated by the carbonic acid, and the filtrate is set aside in a cool place to crystallize. The crystals are carefully washed to remove adhering mother liquor, which contains normal carbonate, a little bicarbonate, chloride, and sulphate of potassium.

Description.—A white salt, crystalline, and soluble in water, but less readily than the mon carbonate. When absolutely pure the reaction is neutral or only very slightly alkaline. By heat it is converted into the mon carbonate with loss

of CO_2 . Dissolved in water it loses carbonic acid even at ordinary temperatures, but rapidly and to complete conversion into normal carbonate above 80°C . (176°F). In the dry state it does not readily part with any of its carbonic acid even at 100°C ., but between 200° and 300°C . it is converted into normal carbonate.

Tests.—Should be completely soluble in water. The solution should not yield a yellowish precipitate with solution of mercuric chloride (carbonate).

The solution acidified with nitric acid should not yield tests for sulphates or chlorides. A platinum wire dipped in a solution of the salt in hydrochloric acid should not show more than a slight yellow color when held in the flame of a Bunsen burner.

Uses.—Potassium bicarbonate is extensively employed in the preparation of other potassium compounds, being both inexpensive and sufficiently pure.

SODIUM CARBONATE.

SODII CARBONAS.



By far the greater portion of *sal sodæ*, or crude sodium carbonate, consumed at this time is prepared by the so-called *Leblanc's method*. A mixture of sodium sulphate, chalk and coal is strongly heated in a reverberatory furnace; the mass is then leached out with water, the solution concentrated, and the carbonate collected as it separates from the hot liquid. The product contains carbonate, sulphide, hydrate, sulphate, and hyposulphite of sodium. The residue obtained by evaporating the first solution to dryness is called *soda-ash*, of which several hundred million pounds are annually imported into the United States. The crude sodium carbonate is purified by re-crystallization.

At Natrona, Pa., near Pittsburg, large quantities of soda are made from *cryolite*, a mineral composed of the fluorides of sodium and aluminium. A mixture of powdered cryolite and chalk is ignited in a furnace, the first reaction being: $6\text{NaF} \cdot \text{Al}_2\text{F}_6 + 6\text{CaCO}_3 = \text{Na}_2\text{O}_6\text{Al}_2 + 6\text{CaF}_2 + 6\text{CO}_2$. The fused mass is powdered and the sodium aluminate leached out by water. A stream of carbonic oxide is conducted through the solution of sodium aluminate, which produces sodium carbonate and aluminium hydrate: $\text{Na}_2\text{O}_6\text{Al}_2 + 3\text{CO}_2 + 3\text{H}_2\text{O} = 3\text{Na}_2\text{CO}_3 + \text{Al}_2(\text{OH})_6$.

A third method consists in treating a solution of sodium chloride with NH_3 and afterwards with CO_2 ; the ammonium bicarbonate gives, with the NaCl , sodium bicarbonate and NH_4Cl . The sodium bicarbonate is then converted into carbonate by heat, after which the product is dissolved and crystallized.

Both the ammonia process and the cryolite process yield purer products than the sodium carbonate made by Leblanc's process.

Uses.—Vast quantities of *sal sodæ* are used in the arts and manufactures and in the household economy. In pharmacy it is used in the preparation of various carbonates, and for the production of sodium compounds.

Description.—Large, nearly transparent crystals, which readily give up a part of their water.

The crystals melt in their water of crystallization below 35° C. They are very readily soluble in water, but not in alcohol. They dissolve quickly in acids, with effervescence.

Tests.—A perfectly clear solution should be formed with water. When this is saturated with nitric acid the addition of silver nitrate or barium nitrate should not produce more than a slight turbidity from chlorides or sulphates.

5.72 Gm. when saturated with pure dilute hydrochloric acid, and evaporated carefully to dryness and strongly heated, should leave a residue weighing nearly 2.386 Gm.

DRIED SODIUM CARBONATE.

SODII CARBONAS EXSICCATUS.



Crushed or coarsely powdered sodium carbonate is allowed to effloresce by exposure to warm air (20° to 25° C.) for several days; then it is heated to 45° C. (113° F.) until it has been converted into a white powder weighing about half as much as the crystallized salt used. Sift the powder and preserve it in a well stoppered bottle.

Sodium carbonate contains 10 molecules of water of crystallization. When exposed to the air it effloresces rapidly, and in the course of one or more weeks, according to the temperature and the dryness of the air, it loses about 40 per cent. of its weight. At 34° C. (93° F.) crystallized sodium carbonate begins to dissolve in its water of crystallization. In preparing dried sodium carbonate this solution in the water of crystallization should be avoided, because afterwards the process of drying becomes more difficult and tedious. Hence it is directed that the salt be exposed to a lower degree of heat for several days before the temperature is raised sufficiently to complete the drying.

At 45° C. the salt loses all but two molecules of its water of crystallization. At 90° to 100° C. it becomes anhydrous.

Pure anhydrous sodium carbonate is most conveniently prepared by heating pure sodium bicarbonate in a silver (or nickel-plated) dish to redness.

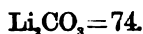
Description.—A white powder, which to the touch appears perfectly dry. It should contain at least 72.6 per cent. of Na_2CO_3 and correspond to tests given for the crystallized salt.

SODIUM BICARBONATE.**SODII BICARBONAS.**

Prepared by saturating a solution of sodium carbonate with carbonic acid gas, or by conducting carbonic acid gas for several days into closed chambers filled with crystallized sodium carbonate. The liberated water of crystallization retains in solution the chloride and sulphate which may have been present in the carbonate.

Description.—A fine white powder which, when absolutely pure, should dissolve in cold water, yielding a neutral solution.

Heat converts it into the monocarbonate.

LITHIUM CARBONATE.**LITHII CARBONAS.**

Prepared from *lepidolite*, a mineral containing silicates and fluorides of lithium, aluminium, small amounts of rubidium and thallium, and traces of caesium.

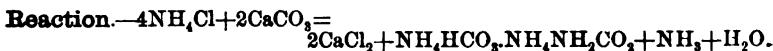
The powdered mineral is first digested with H_2SO_4 , after which the mass is heated until dried. The residue is leached with water, leaving silica behind. On adding potassium sulphate to the solution the aluminium salt is converted into alum, which is crystallized out. The remainder of the aluminium salt is removed by precipitation with calcium hydrate, the filtrate is treated with barium chloride, whereby barium sulphate is thrown down, and the lithium chloride contained in the solution is recovered by evaporating to dryness, dissolving the residue in alcohol, filtering the liquid, distilling off the alcohol, removing the calcium salt with ammonium oxalate, and iron as well as other metals with hydrogen sulphide; the solution is then concentrated and lithium carbonate formed by precipitation with ammonium carbonate and ammonia. The precipitate is washed with 60 per cent. alcohol and dried.

AMMONIUM CARBONATE.**AMMONII CARBONAS.**

[HARTSHORN SALT. SAL VOLATILE.]



Ammonium carbonate, so called, is prepared by sublimation. The materials are either 1 part of ammonium chloride and 2 parts of chalk, or a mixture of 4 parts of ammonium sulphate, 4 parts of chalk, and 1 part of charcoal. The mixture is heated to redness in an iron or stoneware retort, and the vapor is carried into a leaden chamber, where it condenses. The product is purified by resublimation.



Composition.—The preparation consists of one molecule of ammonium carbonate and one molecule of ammonium carbamate. Alcohol dissolves out the ammonium carbamate, leaving the acid ammonium carbonate.

Description.—Usually as large translucent crystalline masses, which lose CO_2 and NH_3 by exposure to the air. The salt has a strong odor of ammonia, and is freely soluble in water.

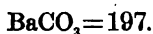
Tests.—It should volatilize completely, leaving no carbon residue from organic matter. The solution of the salt acidified with nitric acid should yield no precipitate with silver nitrate or barium nitrate.

The volumetric determination can be made as explained later.

AROMATIC SPIRIT OF AMMONIA.**SPIRITUS AMMONIÆ AROMATICUS.**

This is a preparation in which the ammonium carbonate of the Pharmacopœia is dissolved in water together with ammonia water enough to form normal ammonium carbonate and ammonium carbamate. This solution is then added to a solution of the volatile oils of lemon, lavender, and pimento in alcohol. The official ammonium carbonate being only partially soluble in alcohol (the carbamate dissolving while the acid carbonate is insoluble) it is necessary to add ammonia water to obtain a permanent solution.

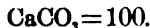
The official process for this preparation directs the use of "alcohol recently distilled and which has been kept in glass vessels." The object of this injunction is to inhibit the use of alcohol kept in barrels of oak, and hence containing traces of tannin sufficient to be discolored by the alkali, as tannin, when acted upon by any alkali, becomes gradually decomposed, yielding dark colored humus. Other organic matters are also darkened by alkalies.

BARIUM CARBONATE.**BARII CARBONAS.**

Prepared by heating to redness a mixture of 10 parts of heavy spar (barium sulphate), 2 parts of charcoal and 5 parts of potassa, and washing the fused mass with water, when the residue is barium carbonate:



It may also be made by precipitating 6 parts of barium chloride with 7 parts of sodium carbonate, and washing and drying the precipitate.

PRECIPITATED CALCIUM CARBONATE.**CALCII CARBONAS PRÆCIPITATUS.**

Solution of calcium chloride.....	220 C.c.
Sodium carbonate.....	180 Gm.
Boiling water	240 C.c.

Dissolve the sodium carbonate in the water. Heat the solution of calcium chloride to about 80° C. (176° F.). Mix the hot solutions, pouring the calcium chloride solution into the soda solution with constant stirring. Wash the precipitate by decantation, then collect and dry it.



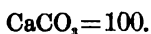
Notes.—A formula for the solution of calcium chloride has been given. When it is desired to make the preparation from calcium chloride, use 10 parts of the fused chloride dissolved in 100 parts of water, and 26 parts of sodium carbonate dissolved in an equal quantity.

Hot solutions are used to insure a dense precipitate, so that the process of washing may be easier; when cold solutions are used the precipitated calcium carbonate is a very bulky magma, difficult to wash free from sodium chloride.

The precipitate should be washed until the washings cease to be rendered turbid by test solution of silver nitrate, and then dried at 100° C. (212° F.).

Description.—A fine white powder, insoluble in water and alcohol. With pure hydrochloric acid it should dissolve to a perfectly colorless fluid. This, when heated to expel CO_2 , and saturated with ammonia water, should not become turbid, showing absence of alumina, iron and phosphates.

The solution of the powder in acetic acid should not be precipitated by solution of potassium bichromate. The solution of the powder in pure dilute nitric acid should not be rendered turbid by silver nitrate or barium nitrate.

PREPARED CHALK.**CRETA PRÆPARATA.**

Triturate 1,000 Gm. of chalk with a little water until reduced to a very fine powder by the "levigation." Throw the mixture into a vessel capable of holding about twenty liters and nearly filled with water, stir the mixture well, and, after a brief time, decant the supernatant liquid, while yet white and turbid from the suspended particles of the finely divided chalk, into another vessel. To the residue in the first vessel add a fresh portion of water, stir well again, and after allowing the coarser particles to subside as before, decant once more, adding the second turbid liquid to that previously decanted. Set the mixed liquors aside, and when the fine powder has subsided perfectly, pour off the water, and collect and dry the powder.

Note.—This process of separating the coarse, gritty particles from the levigated chalk is called "elutriation," the object being to obtain a very soft, finely divided product.

Instead of drying the product as a mass, the moist powder may be formed into cones by "trochiscation."

MAGNESIUM CARBONATE.**MAGNESII CARBONAS.**

Prepared from chloride or from sulphate of magnesium by precipitation with sodium carbonate. The magnesium salts are obtained from the "bittern" of salt-works. Magnesium carbonate is also manufactured from *dolomite*, or magnesian limestone, by dissolving the magnesium carbonate from the powdered mineral by means of cold water and carbonic acid under pressure, when magnesium bicarbonate is formed. The solution is then boiled, when the basic carbonate, which constitutes the official preparation, is precipitated.

In pharmacy distinction is made between "heavy magnesium carbonate" and "light magnesium carbonate." The light magnesium carbonate differs from the heavy variety in these respects: the light carbonate is about three times as bulky; when examined under the microscope, it is found to be partly amorphous, but containing numerous

slender prismatic crystals, whereas the heavy variety is wholly amorphous and somewhat granular; the light magnesium carbonate contains more carbonic acid and yields less magnesium oxide on calcination.

These differences depend upon the methods employed in the preparation of the products. The working formulæ of the British Pharmacopœia are as follows:

LIGHT MAGNESIUM CARBONATE.

MAGNESII CARBONAS LEVIS; B.

Magnesium sulphate	25 parts.
Sodium carbonate	30 parts.

Dissolve each salt in 200 parts of cold distilled water, filter, and mix the solutions *cold*. Boil the mixture in a porcelain dish for fifteen minutes. Transfer the precipitate to a wetted muslin strainer, and wash it with boiling distilled water until the washings cease to give a precipitate with test solution of barium chloride. Then let the precipitate drain, and dry it at not over 100° C. (212° F.).

HEAVY MAGNESIUM CARBONATE.

MAGNESII CARBONAS PONDEROSUS; B.

Magnesium sulphate	25 parts.
Sodium carbonate	30 parts.

Dissolve the salts, each in 50 parts of boiling distilled water; filter, and mix the two solutions while *hot*. Evaporate the mixture on a sand-bath to perfect dryness. Digest the residue for half an hour with 100 parts of boiling water, collect the precipitate on a wetted muslin strainer, and wash it repeatedly with distilled water until the washings cease to give a precipitate with test solution of barium chloride. Drain the product and dry it at not over 100° C. (212° F.).

Reaction.— $4\text{MgSO}_4 + 4\text{Na}_2\text{CO}_3 + 5\text{H}_2\text{O} = 3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O} + 4\text{Na}_2\text{SO}_4 + \text{CO}_2$; or perhaps $5\text{MgSO}_4 + 5\text{Na}_2\text{CO}_3 + 6\text{H}_2\text{O} = 4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O} + 5\text{Na}_2\text{SO}_4 + \text{CO}_2$.

Notes.—It will be seen that the differences in manipulation are: the use of more dilute and cold solutions in making the light magnesium carbonate, and the precipitate is in that case simply heated for fifteen minutes with the mother liquor; while, in making the heavy magnesium carbonate, the solutions are four times as concentrated, and mixed while hot, the mixture being then evaporated to perfect dryness on a sand-bath, after which the residue is freed from sodium sulphate by digestion and subsequent washing with boiling water.

When the precipitate is formed with cold solutions, it contains more carbonic acid than if prepared with hot solutions. When boiled in the liquid for a short time carbonic acid passes away; in preparing the light magnesium carbonate the

heating should be discontinued as soon as the evolution of carbonic acid has commenced. When formed with hot, concentrated solutions, the mixture being boiled down to dryness, the precipitate contains less carbonic acid when formed, and loses more of that acid afterwards when exposed to the stronger heat.

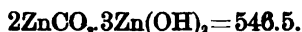
Composition.—Fritzsche, Hager and Flückiger state that the composition of magnesium carbonate is $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O} = 468$; the U. S. P. gives it as $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O} = 486$; the British Pharmacopœia states it as being $8\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O} = 384$; That there is a difference in composition between light and heavy magnesium carbonate may be regarded as certain, although the same formula is given by the British Pharmacopœia for both. Light magnesium carbonate contains a greater proportion of true carbonate (MgCO_3) and a correspondingly less proportion of hydrate ($\text{Mg}(\text{OH})_2$). The quantity of water in the compound seems also to vary.

Description.—A light white mass or powder, nearly insoluble in water, but dissolving readily in dilute acids.

Tests.—The solution in nitric acid should be perfectly clear, and when treated with silver nitrate or barium nitrate, should give no precipitate or turbidity. Ammonia water precipitates this solution, but it should dissolve the precipitate fully when added in excess.

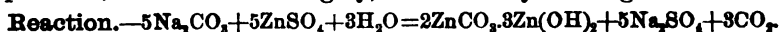
PRECIPITATED ZINC CARBONATE.

ZINCI CARBONAS PRÆCIPITATUS.



Zinc sulphate 20 parts.
Sodium carbonate 21 parts.
Boiling water, sufficient.

Dissolve the sodium carbonate in 40 parts of the water in a porcelain capsule. Dissolve the zinc sulphate in an equal quantity of boiling water. Place the capsule containing the solution of sodium carbonate on a sand-bath so as to keep the solution hot; then gradually add the solution of zinc sulphate, stirring briskly. Boil the mixture for fifteen minutes after the effervescence has ceased; then let the precipitate subside. Decant the mother liquor and throw it away. Add 120 parts of boiling water to the precipitate, and stir well, let settle once more, and repeat the washing by affusion and decantation of hot distilled water until the washings cease to give any precipitate with test solution of barium chloride. Collect the precipitate on a muslin strainer or on a paper filter, let it drain thoroughly, and then dry it at a gentle heat.



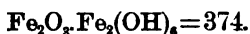
Notes.—The solutions are used hot in order to expel all the carbonic acid which is set free, carbon dioxide escaping with effervescence. If cold solutions are used a portion of the precipitate redissolves in the carbonic acid held in the liquid. The zinc sulphate is to be added to the sodium carbonate in order to keep the latter in excess, and by having the soda solution hot, the further advantage is gained that the precipitate is more readily washed free from sodium salt.

Description.—A light, soft, white powder, insoluble in water but readily soluble, with decomposition, in dilute acids. When strongly heated it gives off CO_2 , leaving the oxide.

Tests.—It should give nothing to water, but should yield a perfectly clear solution with hydrochloric or sulphuric acid.

SUBCARBONATE OF IRON.

FERRI SUBCARBONAS; U. S. P., 1870.



Ferrous sulphate 8 parts.

Sodium carbonate 9 parts.

Dissolve the salts, each in 40 parts of boiling water, filter, and pour the solution of iron sulphate into that of the sodium carbonate, with constant stirring. Wash the precipitate with cold water, first by decantation and afterwards on a muslin strainer, until the washings cease to be precipitated by test solution of barium chloride. Then drain, and dry the precipitate without heat.

Reaction.— $\text{FeSO}_4 + \text{Na}_2\text{CO}_3 = \text{FeCO}_3 + \text{Na}_2\text{SO}_4$. The ferrous carbonate oxidizes, as explained in the note.

Notes.—To insure that the sodium carbonate is in excess over the ferrous sulphate, which is necessary to insure complete double decomposition, add that to the iron salt. The solutions should be boiling in order that the ferrous carbonate formed may be heavy, and also to prevent the formation of soluble bicarbonate. When cold solutions are used a portion of the precipitate, which is at first nearly white, soon decomposes, losing a portion of its carbonic acid, which combines with another portion of ferrous carbonate and holds it in solution as bicarbonate. After a time this, too, decomposes, the carbonic acid being liberated and ferric hydrate being formed by the absorption of oxygen from the air. When hot solutions are used the carbonic acid is rapidly expelled and the perfect precipitation of the iron compound not retarded. Owing to gradual oxidation the precipitate rapidly changes color in contact with the air, passing through various shades of gray, green, blue, olive, brown, and red. The gray, green, blue and olive are due to ferrosferric hydrate, while the brown and red are caused by ferric hydrate. Finally, the precipitate becomes almost completely ferric. Dried at high heat the preparation is more red, and less readily soluble in hydrochloric acid.

The ferric hydrate generally rises to the surface of the mixed liquids, and during the washing of the precipitate the surface of the magma becomes covered with it, while the interior continues bluish gray or green. The washing is best effected with boiling water, and on a muslin filter. The pores of the filter-paper become rapidly closed by yellowish red ferric hydrate.

Dried at ordinary temperatures the preparation is olive brown with a reddish tint, retaining a small amount of ferrous carbonate, and is easily powdered. Dried with the aid of considerable heat the product is brown red, and cakes together in hard lumps, which are not so readily powdered.

Description.—A reddish brown or olive brown powder, insoluble in water but soluble in dilute acids, giving off CO_2 in slight amount.

Tests.—The solution in hydrochloric acid should give a blue color with both ferrocyanide and ferricyanide of potassium, but should give no test for sulphates with barium chloride.

SACCHARATED CARBONATE OF IRON.

FERRI CARBONAS SACCHARATUS.

Ferrous sulphate	20 parts.
Sodium bicarbonate.....	15 parts.
Sugar, in fine powder	32 parts.

Dissolve the ferrous sulphate in 80 parts of boiling distilled water, and the sodium bicarbonate in 200 parts of boiling distilled water. Put the hot bicarbonate solution into a flask capable of holding 1,000 parts of water; then add the hot solution of ferrous sulphate, agitating the mixture well, and when the effervescence has subsided fill the flask at once with boiling distilled water, cork it to exclude air, and set it aside for two hours. Then remove the mother liquor by means of a siphon, and again fill the flask with boiling distilled water, shake it well, let it settle once more, and repeat the washing in the same manner until the wash water produces but little turbidity with test solution of barium chloride. Then transfer the precipitate to a wetted muslin strainer, let it drain, or press out the water, and mix the magma intimately with the sugar in a porcelain dish, evaporate the mixture to dryness by means of a water-bath, powder the product, and keep it in a tightly corked bottle.

Reaction.— $\text{FeSO}_4 + 2\text{NaHCO}_3 = \text{FeCO}_3 + \text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{CO}_2$.

Notes.—All the precautions directed by this formula are intended to prevent the oxidation of the precipitate by contact with the air. Sodium bicarbonate is substituted for the normal carbonate in order that the escaping carbonic acid may help to exclude the air. If about 5 parts of sugar be added to the solution of bicarbonate of sodium before the iron salt is poured into it, and if the wash water also be sweetened with about four per cent. of sugar, the oxidation is still more effectually prevented. Boiling water is used in order that no air may be contained in it; and the whole process must be expeditiously carried to its completion in order not to expose the product to oxidation longer than necessary. When the precipitate has been mixed with the sugar, the mixture should not be stirred any more than is necessary during the process of its evaporation to dryness, and as soon as the mass is sufficiently dry it should be at once powdered and put into small bottles, which are to be immediately and tightly closed.

Hager recommends the use of milk sugar instead of cane sugar to facilitate the drying.

A more dense precipitate is obtained by having the solutions hot when mixed.

Sugar and honey aid in preventing oxidation, by excluding the air from the product.

See also the notes under the title, Mass of Carbonate of Iron.

Description.—A grayish powder, which oxidizes on exposure to the air. When treated with water the sugar dissolves.

Tests.—The powder is soluble in hydrochloric acid with effervescence. Heated in the air the sugar burns, and the residue turns to ferric oxide.

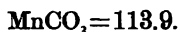
MASS OF CARBONATE OF IRON.**MASSA FERRI CARBONATIS.**

[PILL OF CARBONATE OF IRON. VALLET'S MASS.]

Ferrous sulphate.....	100 parts.
Sodium carbonate.....	110 parts.
Clarified honey.....	38 parts.
Sugar, in coarse powder.....	25 parts.
Syrup, distilled water, each sufficient.	

Dissolve the sulphate of iron and the carbonate of sodium separately, each in two hundred parts of boiling distilled water, and, having added twenty-five parts of syrup to the solution of the iron salt, filter both solutions. Mix when cold, in a bottle just large enough to hold the mixture, or add enough distilled water to fill it; cork the bottle well, and set it aside, that the carbonate of iron may settle. Pour off the supernatant liquid, and, having mixed syrup and distilled water in the proportion of one part of syrup to sixteen parts of water, wash the precipitate with the mixture until the washings no longer have a saline taste. Drain the precipitate on a flannel cloth, and express as much of the water as possible. Lastly, mix the precipitate immediately with the honey and sugar, and, by means of a water-bath, evaporate the mixture, constantly stirring, until reduced to one hundred parts.

Notes.—The reaction is given under the title, Subcarbonate of Iron. Compare this process with that for saccharated carbonate of iron. Sodium bicarbonate should be used here as well as in the preceding preparation instead of the normal carbonate; 75 parts of bicarbonate should be substituted for the 110 parts of carbonate. The use of hot solutions renders the precipitate more dense, which is of material advantage in the preparation of saccharated ferrous carbonate and Vallet's mass, where expeditious washing is necessary.

MANGANOUS CARBONATE.**MANGANI CARBONAS.**

Manganous sulphate.....	22 parts.
Sodium bicarbonate.....	17 parts.

Dissolve the bicarbonate in 200 parts of boiling water; add the sulphate previously dissolved in 100 parts of boiling water and sweetened with 5 parts of sugar. Wash the precipitate with boiling water containing about 4 per cent. of sugar. When the washings give but a slight

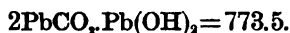
turbidity with test solution of barium chloride, press the water out of the magma, and dry it as rapidly as practicable, with the aid of moderate heat.

Description.—A dirty white powder with a reddish tinge. It is practically insoluble in water, but dissolves in dilute acids.

The solution in hydrochloric acid may be employed for the tests of purity and identity.

LEAD CARBONATE.

PLUMBI CARBONAS.



Prepared by acting on sheet lead with acetic acid, moisture and carbonic acid gas, until the lead is consumed or covered with a thick coat of *white lead*, which is then removed, ground with water, washed and dried. Or, carbonic oxide is conducted through solution of subacetate of lead, the precipitate being the product, while the remaining liquor containing normal lead acetate is again converted into solution of subacetate of lead by maceration with levigated litharge.

White lead is a basic carbonate, as may be seen from the formula given above.

Normal lead carbonate is obtained when lead nitrate or normal lead acetate is decomposed by sodium carbonate.

Description.—A heavy, white powder, insoluble in water, but soluble with effervescence in acetic or nitric acid.

The powder blackens on exposure to an atmosphere containing hydrogen sulphide.

BISMUTH SUBCARBONATE.

BISMUTHI SUBCARBONAS.



Bismuth, in small pieces	500 Gm.
Nitric acid	1,500 C.c.
Ammonia water	1,250 C.c.
Sodium carbonate	2,500 Gm.

Mix 800 C.c. of the nitric acid with 1,000 C.c. of distilled water in a capacious glass vessel, add the bismuth, and set aside for twenty-four hours to dissolve. Dilute the solution with 2,500 C.c. of distilled water (until permanent turbidity results), stir well, again set the liquid aside

for twenty-four hours, and then filter. Dilute the filtrate by gradually adding to it 16,000 C.c. of distilled water, and mixing well. Now add, slowly, the ammonia water through a small siphon, stirring constantly and actively. Transfer the whole to a wetted muslin strainer, and let drain. When the liquid has drained off pour upon the precipitate 8,000 C.c. of distilled water, mixing well, and then let drain again. Now transfer the precipitate to a suitable vessel, add the remainder of the nitric acid, and, when all has dissolved, also add gradually 1,000 C.c. of distilled water, and set the solution aside for twenty-four hours. Then filter.

Dissolve the sodium carbonate in 3,000 C.c. of distilled water, with the aid of heat, filter the solution, and set it aside until cold. Now pour the cold solution of bismuth nitrate very slowly into the solution of sodium carbonate, with constant and brisk stirring. Transfer the whole to a wetted muslin strainer, and, after draining thoroughly, wash the precipitate with distilled water, as expeditiously as practicable, until the washings become tasteless. Lastly, press out the moisture as far as practicable, dry the precipitate on bibulous paper, or on muslin, at a gentle heat, and then powder it by rubbing it through a fine sieve by means of a soft brush.

Reaction.—First a solution of bismuthous nitrate is made: $2\text{Bi} + 8\text{HNO}_3 = 2\text{Bi}(\text{NO}_3)_3 + 2\text{NO} + 4\text{H}_2\text{O}$.

This is poured into a large quantity of water containing ammonia, whereby basic bismuthous nitrate is thrown down, the ammonia being added to neutralize the free nitric acid so as to prevent it from retaining any bismuth nitrate in the liquid. Then the precipitate is redissolved in nitric acid to form again the $\text{Bi}(\text{NO}_3)_3$. Finally, $2\text{Bi}(\text{NO}_3)_3 + 8\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} = (\text{BiO})_2\text{CO}_3 \cdot \text{H}_2\text{O} + 6\text{NaNO}_3 + 2\text{CO}_2$.

Notes.—As the bismuth usually contains arsenic the acid solution first prepared contains bismuth arsenate; when the liquid is diluted with water until permanently somewhat turbid, the arsenical salt precipitates before the bismuth nitrate does, and hence, after twenty-four hours' rest, most of the arsenate is found deposited as a white precipitate, and is then filtered away. The rest of the arsenic remains in the mother liquor after the precipitation of the bismuth nitrate with ammonia, as ammonium arsenate. See also the notes under the title, Sub-nitrate of Bismuth.

Description.—A soft, white powder, which becomes converted into yellow oxide by heat. It is quite insoluble in water, but should give a clear solution with nitric acid.

CHAPTER XX.

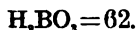
BORATES.

Borax is the only borate used in medicine or pharmacy.

BORIC ACID.

ACIDUM BORICUM.

[BORACIC ACID.]



Occurs in considerable quantity in nature, in a free state, especially in Tuscany and in the western portions of North America. In some localities in Tuscany there are jets of steam issuing from the ground, and this steam carries boric acid with it, which is obtained by condensing the vapors, concentrating the solution, and crystallizing. In the United States, west of the Rocky Mountains, the waters of many hot springs contain boric acid. The impure boric acid from these sources is used chiefly in the manufacture of borax, which is purified by recrystallization. Pure boric acid can be readily made from refined borax, as follows:

Borax, in powder	5 parts.
Hydrochloric acid	3 parts.

Dissolve the borax in 12 parts of boiling distilled water and add the hydrochloric acid to the hot solution, stirring it. Set aside until cool, when crystals of boric acid will deposit. Collect the crystals upon a filter and wash them with a little cold distilled water; then redissolve them in 14 parts of boiling distilled water, filter while hot, and set

aside to cool. Collect the crystals on a filter, and dry them between blotting paper.

More crystals may be recovered from the mother liquor on evaporation.

Reaction.— $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} = 4\text{H}_3\text{BO}_3 + 2\text{NaCl}$.

Notes.—The yield is about $2\frac{1}{4}$ parts. Hydrochloric acid is employed in preference to sulphuric acid, because it is comparatively easy to drive off or wash away any free HCl; but sulphuric acid can be gotten rid of only with great difficulty, if at all.

Properties.—White, six-sided plates, slightly unctuous to the touch, permanent in the air, odorless, having a cooling, bitterish taste, and a feebly acid reaction; the solution turns blue litmus paper red and turmeric paper brown, the tint, in the latter case, remaining unaltered in presence of free hydrochloric acid. Boric acid is soluble in 25 parts of water and in 6 parts of alcohol at 15°C . (59°F .); in 3 parts of boiling water and in 5 parts of boiling alcohol. On ignition, boric acid loses 43.5 per cent. of its weight, and, on cooling, becomes transparent and brittle. The alcoholic solution burns with a flame tinged with green.

Uses.—It is a very powerful antiseptic, and hence of great value, being at the same time non-irritant and quite innocuous. As an antiseptic it is used either in solution or in extremely fine powder.

Tests.—An aqueous solution of boric acid should not be precipitated by test solutions of chloride of barium (sulphate), nitrate of silver with nitric acid (chloride), sulphide of ammonium (lead, copper, iron, etc.), or oxalate of ammonium (calcium). A fragment heated on a clean platinum wire in a non-luminous flame should not impart to the latter a persistent yellow color (sodium salt).

BOROGLYCERIDE.

[GLYCERYL BORATE.]

Boric acid, in fine powder 6 parts.
Glycerin 9 parts.

Heat together in a porcelain dish at 150°C . (302°F .), stirring well until aqueous vapors cease to be given off, and a homogeneous transparent mass is formed, which becomes hard and tough on cooling.

Notes.—Care should be taken not to heat the mixture too strongly, as that would render the product dark colored.

Boroglyceride is a colorless, tough, solid substance, soluble in water and in alcohol.

SODIUM BORATE.

SODII BORAS.

[BORAX.]

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} = 382$.

Borax occurs native in Persia, Thibet, and other western Asiatic countries, and in large deposits in California and Nevada, either alone or with other borates. Most of the borax now used is made from crude

boric acid by fusion with dried sodium carbonate, solution in water, and crystallization.

Description.—Large crystals or fine white powder, completely soluble in water. The crystals become anhydrous on strongly heating, increasing greatly in bulk.

GLYCERITE OF BORAX.

GLYCERITUM BORACIS.

Borax, in fine powder	30 Gm.
Glycerin	120 C.c.
Distilled water	60 C.c.

Mix in a porcelain capsule and heat gently on a water-bath until dissolved.

Notes.—This preparation becomes acid and unfit for use in a short time, by some chemical change. It has been stated that free boric acid is contained in it.

SILICATES.

Many important natural substances are silicates, such as the clays, felspars, soapstones, etc., and among artificial products, consisting essentially of silicates, may be mentioned the various kinds of glass, porcelain ware, crockery, bricks, etc.

Several varieties of glass are distinguished. The most important are :

1°. *Bohemian glass.*—This is chiefly a mixture of potassium and calcium silicates. It is hard, becomes soft only at high temperatures, and is not readily attacked by chemical reagents. It is the best glass for beakers, flasks and other chemical ware.

2°. *Bottle glass.*—This is a mixture of silicates of sodium, calcium, iron and aluminium, and as a rule the materials are not selected with great care. It is much softer than the preceding and more readily attacked by reagents, especially by acids and alkalies.

3°. *Crown or window glass.*—This, like bottle glass, contains silicates of sodium, calcium, iron and aluminium; but the last two are in small amount, while the sodium silicate is more abundant than in bottle glass.

4°. *Flint glass.*—Is essentially a lead and potassium silicate. It is easily melted, heavy, has a bright luster, but is very much attacked by reagents.

Lead glass is sometimes made into ware for chemical use, but it should never be employed in contact with solutions, and is consequently quite unfitted for reagent bottles.

It answers well, however, for tubing used for connections and in manipulations with gases, being readily bent.

The following table gives the composition of several kinds of glass:

	SiO ₂	K ₂ O	Na ₂ O	CaO	MgO	PbO	Fe ₂ O ₃	Al ₂ O ₃
Bohemian	71.70	12.70	2.50	10.80	-----	-----	.90	
Bohemian	76.00	15.60	-----	8.00	-----	-----	1.00	
Bohemian	73.13	11.49	3.07	10.43	.26	-----	.89	
German crown	73.11	-----	13.00	13.24	-----	-----	.83	
English crown	71.40	-----	15.00	12.40	-----	-----	.60	
English window	70.71	-----	13.25	13.88	-----	-----	1.92	
Germ.hollow glass	78.39	-----	13.91	7.10	-----	-----	.60	
French hollow glass	72.00	-----	17.00	6.50	-----	-----	4.50	
German bottle	65.57	2.72	4.86	20.42	-----	-----	2.81	3.34
French bottle	59.60	8.20	-----	18.00	7.00	-----	4.40	6.80
English flint	51.40	9.40	-----	-----	-----	87.40	2.00	
French flint	50.18	11.22	-----	-----	-----	88.11	0.44	

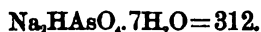
CHAPTER XXI.

ARSENATES.

The soluble sodium arsenate and insoluble ferrico-ferrous arsenate are the only ones employed.

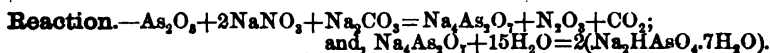
SODIUM ARSENATE.

SODII ARSENAS.



Arsenous oxide	20 parts.
Sodium nitrate	17 parts.
Dried sodium carbonate	11 parts.

Powder these substances and mix them intimately by trituration. Heat the mixture in a large covered clay crucible at a red heat until effervescence has ceased, and complete fusion takes place. Let the fused mass solidify on a porcelain surface, and, while still warm, put it into 85 parts of boiling distilled water, and stir until dissolved. Filter while hot, and set aside to crystallize. Collect, drain, and dry the crystals, and keep them in a tightly corked bottle.



Notes.—The residue after the process of heating the mixture is pyroarsenate of sodium, which is converted into orthoarsenate by water.

A more convenient process is to dissolve the arsenous oxide in 125 parts of solution of soda, evaporating to dryness, and fusing the residue with the sodium nitrate.

When crystallized at a low temperature sodium arsenate has 12 molecules of water of crystallization; at ordinary temperature it usually crystallizes with 7H₂O; in dry air it effloresces, losing 5H₂O; the last of the water is driven off at about 149° C. (300° F.); and when heated to redness it becomes converted into pyroarsenate, which, however, when dissolved in water becomes immediately converted back into arsenate.

Description.—Large, colorless prisms, which effloresce in dry air. They are soluble in water, and the solution has a slight alkaline reaction.

SOLUTION OF SODIUM ARSENATE.

LIQUOR SODII ARSENATIS.

Sodium arsenate, dried at 149° C.	1 part.
Distilled water	99 parts.

Notes.—Owing to the variable amount of water of crystallization found in the sodium arsenate of commerce, the Pharmacopœia directs that the salt should be heated at 149° C. (300° F.) until deprived of all its water of crystallization before it is weighed out, and used in making the official solution. See preceding paragraph.

IRON ARSENATE.

FERRI ARSENAS.

Ferrous sulphate	46 parts.
Sodium arsenate, dried at 149° C.	35 parts.
Sodium bicarbonate	10 parts.

Dissolve the sodium arsenate in 200 parts of boiling distilled water, and the ferrous sulphate in 240 parts of boiling water; add the solution of the iron salt to that of the arsenate; then add the solution of sodium

bicarbonate previously dissolved in 120 parts of boiling water. Stir well. Collect the precipitate on a wetted muslin strainer and wash it with water until the washings cease to be affected by test solution of barium chloride. Squeeze the washed precipitate, folded in strong linen, in a screw press, and dry it on porous bricks in a warm air chamber at a temperature not exceeding 40° C. (104° F.).

Notes.—The reaction is analogous to that occurring in the process of preparing the precipitated ferroso-ferric phosphate. The precipitate is ferroso-ferric arsenate, of variable composition and color.

Description.—A green to greenish blue powder insoluble in water and alcohol. It contains about 26 per cent. of water of crystallization, most of which is given off at a temperature of 100° C.

The solution in hydrochloric acid gives a yellow precipitate with hydrogen sulphide.

ARSENITES.

Fowler's solution contains potassium arsenite. This is the only arsenite of pharmacy.

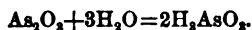
SOLUTION OF ARSENOUS ACID.

LIQUOR ACIDI ARSENOSI.

Arsenous oxide	1 part.
Hydrochloric acid	2 parts.
Distilled water	97 parts.

Boil the arsenous oxide with the acid diluted with 25 parts of the water until dissolved. Filter the solution, and pass enough distilled water through the filter to make the product weigh 100 parts.

Notes.—The presence of hydrochloric acid materially aids the solution of the arsenous oxide. When dissolved in the water the oxide is probably converted into arsenous acid:



This preparation was formerly erroneously called "solution of chloride of arsenic;" no chemical reaction seems to take place between either arsenous oxide or arsenous acid and hydrochloric acid in solution.

Description.—A colorless solution with an acid reaction. It gives a bright yellow precipitate with hydrogen sulphide.

Tests.—The strength of the solution is best ascertained by means of standard iodine solution, after boiling with solution of sodium bicarbonate.

SOLUTION OF POTASSIUM ARSENITE.**LIQUOR POTASSII ARSENITIS.****[FOWLER'S SOLUTION.]**

Arsenous oxide	1 part.
Potassium bicarbonate	1 part.
Compound tincture of lavender	3 parts.
Distilled water	95 parts.

Boil the arsenous oxide and the potassium bicarbonate in a flask with 10 parts of distilled water until completely dissolved. Then add the tincture, and finally enough distilled water to make the product 100 parts. Set the liquid aside for eight days and then filter through paper.

Reaction.— $\text{As}_2\text{O}_3 + 4\text{KHCO}_3 = 2\text{KH}_2\text{AsO}_3 + \text{H}_2\text{O} + 4\text{CO}_2$.

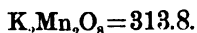
Notes.—It has been observed that when solution of arsenite of potassium is long kept, a small amount of arsenous oxide gradually separates. In one case as much as 15 per cent. of the amount originally dissolved had separated in the course of three years. It is probable that this is the result of the absorption of carbonic acid from the air whereby the arsenite is broken up, after which the arsenous acid passes into the less soluble crystalline modification of arsenous oxide. The possibility of there being precipitated arsenous oxide in the preparation renders it necessary to examine it from time to time, when it is to be dispensed, and to filter it occasionally. Still better is to prepare a fresh lot every six months. No separation of arsenous oxide is likely to occur in eight days, so that the precaution prescribed in the Pharmacopœial working formula is superfluous.

Description.—A reddish solution with slight alkaline reaction. It should not give a precipitate with hydrogen sulphide until after addition of hydrochloric acid.

The strength of the liquid may be determined by means of volumetric iodine solution, described later.

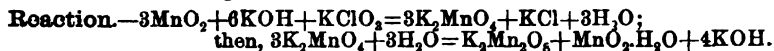
PERMANGANATES.

Permanganate of potassium is the one important permanganate.

POTASSIUM PERMANGANATE.**POTASSII PERMANGANAS.**

Potassa	50 Gm.
Black oxide of manganese, in fine powder	40 Gm.
Potassium chlorate, in fine powder	35 Gm.
Distilled water	500 C.c.
Carbonic acid, sufficient.	

Mix the oxide and the potassium chlorate; put the mixture in a porcelain capsule; add the potassa, previously dissolved in 40 C.c. of water. Evaporate the mixture to dryness on a sand-bath, stirring diligently to prevent spurting. Powder the residue, put it in a covered crucible, and expose it to a dull red heat for one hour, or until it has assumed a semi-fused condition. Let it cool, powder, and boil it with 800 C.c. of water. Let the insoluble matter subside and decant the liquid; boil the residue again with 100 C.c. of water and again decant. Mix the decanted liquids, saturate the mixture with carbonic acid, and then evaporate until a pellicle forms. Set aside to cool and crystallize. Drain the crystalline mass, boil it in 60 C.c. of water, and strain through a little asbestos placed in the throat of a funnel. Let cool and crystallize, drain the crystals and dry them by placing them under a bell-jar over a vessel containing sulphuric acid.



Notes.—The carbonic acid is introduced to convert the potassium hydrate into carbonate, which is necessary because the manganese peroxide cannot be completely converted into permanganate in the presence of potassium hydrate.

Description.—Dark purple crystals with peculiar greenish luster. A very small amount of the salt is capable of imparting a deep purple color to a large volume of water. This is not permanent in presence of organic matter and other reducing agents. The solution is a valuable reagent in volumetric analysis, and will be described later.

PREPARATIONS WITH ORGANIC ACIDS.

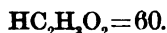
CHAPTER XXII.

ACETATES.

All are water soluble. Many of them may be prepared by neutralizing acetic acid with the hydrates, carbonates, or oxides of the metals. Others are made by double decomposition.

ACETIC ACID.

ACIDUM ACETICUM.



Formerly prepared by acetic fermentation of dilute alcohol, or of weak saccharine liquids. It is now made by dry distillation of wood. Oakwood billets are heated in closed sheet-iron cylinders, one of the numerous products being impure acetic acid, or *wood vinegar*, which is afterwards purified.

The impure acetic acid obtained by the destructive distillation of wood is called pyroligneous acid, and has a disagreeable smoky odor from the empyreumatic products contained in it. Even the purer grades of acetic acid contain empyreumatic matters, and only chemically pure acid is entirely free from them. To get rid of these impurities the acid is treated with lime and soda, the acetates of calcium and sodium are

freed from the tarry matters, and then decomposed by sulphuric or hydrochloric acid. A nearly pure acetate of sodium can thus be made from the impure acid, and by distilling a mixture of this sodium acetate with sulphuric acid a purer grade of acetic acid is obtained, which can be further purified by again neutralizing with sodium carbonate, decomposing the acetate with sulphuric acid, and distilling as before. A pure sodium acetate is finally obtained, from which pure acetic acid may be made as follows:

Sodium acetate..... 18 parts.
Sulphuric acid..... 13 parts.

Reduce the acetate to a coarse powder; introduce it into a distilling flask; warm the flask; connect it with a condenser and receiver; add the sulphuric acid through a funnel tube, a little at a time, and continue the distillation until 12 parts of distillate have been collected. Dilute this product with distilled water until it has the specific gravity desired.

Test the acid with volumetric solution of soda to determine its percentage strength.

Properties.—A watery solution composed of 36 per cent. of hydrogen acetate and 64 per cent. of water.

A clear, colorless liquid, of a distinctly vinegar-like odor, a purely acid taste, and a strongly acid reaction. Sp. gr. 1.048 at 15° C. (59° F.), compared with water at +4° C. (39° 2 F.) as 1.000. Its specific volume is accordingly 0.954. Miscible in all proportions with water and alcohol, and wholly volatilized by heat. Acetic acid neutralized with water of ammonia, is colored deep red by ferric chloride, and decolorized again by strongly acidulating with sulphuric acid.

At 22° C. (71° 6 F.) the official acetic acid has the specific gravity 1.0458 compared with water at the same temperature as a constant. By Beaumé's scale this acid is 6° 8.

Tests.—Acetic acid should not yield a precipitate with hydrogen sulphide (lead, copper or tin), or when supersaturated with water of ammonia (iron), or with test solution of oxalate of ammonium (calcium). When slightly supersaturated with water of ammonia, the liquid should not exhibit a blue tint (copper), nor should any residue be left on evaporating this alkaline liquid on the water-bath (other acids and fixed impurities). When supersaturated with solution of potassa it should not have a smoky odor or taste, and when diluted with 5 volumes of distilled water, the color caused by the addition of a few drops of test solution of permanganate of potassium should not be sensibly changed by standing five minutes at the ordinary temperature (abs. of empyreumatic substances). Boiled with an equal volume of sulphuric acid, the liquid should not be darkened (organic impurities). On adding a crystal of ferrous sulphate to a cooled mixture of equal volumes of acetic and sulphuric acids, no brown or reddish brown zone should make its appearance around the crystal (nitric acid). No precipitate should be formed on the addition of a few drops of test solution of chloride of barium (sulphuric acid), nor by adding to another portion some test solution of nitrate of silver (hydrochloric acid), nor, after the last-named addition, should the mixture turn dark on warming (sulphurous acid).

To neutralize 6.0 Gm. of acetic acid should require 36 C.c. of normal sodium hydrate solution.

The empyreumatic matters, if present in smaller quantities, cannot be detected by their odor because masked by the odor of the acid itself; but when the acetic acid is neutralized the smoky odor will at once become distinct unless the acid is almost entirely free from empyreuma. The permanganate test is regarded as too severe when applied according to the Pharmacopoeial directions. Dr. Squibb (*Ephemeris*, March, 1888) advises the following method of applying this test: Add 1 C.c. of the acid to 5 C.c. of distilled water in a test tube;

mix by pouring the liquid from one test tube to the other, and not by closing the tube with the finger and shaking, as that might often vitiate the test; put 6 C.c. of distilled water in another test tube, to be put beside the first for comparison; now put three drops of decinormal permanganate solution in each tube, and mix well by pouring back and forth between two test tubes as before. By comparing the color of the liquid containing the acid with that of the liquid without acid, the change of color in the first may be readily observed. An acid which will not wholly change the permanganate color to brown with three drops of the test solution within ten minutes may be considered as a very good acid so far as regards freedom from empyreumatic products.

The volumetric test is a safer test of the strength of acetic acid than the indication afforded by its specific gravity. It is best applied as follows: Weigh 6 Gm. of the acid in a beaker; add two or three drops of solution of phenolphthalein, and then add the soda solution from a graduated burette, stirring well after each addition, until the liquid suddenly acquires a pink color.

When phenolphthalein and a graduated burette are not at hand, the acid may be neutralized with potassium bicarbonate as follows: Dissolve 10 Gm. of crystallized potassium bicarbonate in 80 Gm. of distilled water in a tared flask, and make up the weight to 100 Gm. by adding more water. Weigh 6 Gm. of acetic acid into a flask of not less than 4 fluidounces capacity. Now add the potassium bicarbonate solution, a little at a time, to the acid, until the effervescence caused by each addition nearly ceases. Then heat the nearly saturated acid to boiling, and while hot, add to it cautiously from the potassium bicarbonate solution until red litmus paper,—fragments of which are to be dropped into the flask from time to time,—is turned blue by the liquid. Then weigh the remainder of the solution of potassium bicarbonate to ascertain how much has been used. Each Gm. used of this solution corresponds to one per cent. of absolute acetic acid, and, therefore, a 86 per cent. acetic acid would require fully 86 Gm. of the solution of potassium bicarbonate to saturate it. If less or more is required the acid is proportionately weaker or stronger.

Strength.—The various official acetic acids compare as follows:

Pharmacopœia.	Per cent. of $\text{HC}_2\text{H}_3\text{O}_2$.	Sp. gr. 15°	Number of parts representing 60 parts of $\text{HC}_2\text{H}_3\text{O}_2$.
France (1884).....	50	1.060	120
U. S. (1883).....	86	1.048	167
Great Britain (1885).....	83	1.044	182
Germany (1882).....	80	1.041	200
Russia (1880).....	29.41	1.040	204

Composition.—Absolute acetic acid contains 98.33 per cent. of $\text{C}_2\text{H}_3\text{O}_2$ (the acetic acid radical) and 1.67 per cent. of replaceable H. 100 parts of the official (U. S.) acetic acid (86 per cent.) contains 85.40 per cent. of $\text{C}_2\text{H}_3\text{O}_2$.

Uses.—For the preparation of other acetates, diluted acetic acid, etc. Also in a diluted state, as a solvent for alkaloids, volatile oils, acrid substances, etc.

Saturating power.—100 parts of the official (U. S.) acetic acid, containing 86 per cent. of $\text{HC}_2\text{H}_3\text{O}_2$, will saturate alkalies as follows:

Potassa (90 per cent.), 37.33 parts.....	} Yielding 58.80 parts of potassium acetate.
Solution of potassa (5 per cent.), 672 parts.....	
Potassium carbonate (81 per cent.), 51.11 parts.....	
Potassium bicarbonate, 60 parts.....	
Soda (90 per cent.), 26.66 parts.....	} Yielding 81.60 parts of sodium acetate.
Solution of soda (5 per cent.), 480 parts.....	
Sodium carbonate (96 per cent.), 89.38 parts.....	
Sodium bicarbonate (99 per cent.), 50.91 parts.....	
Ammonia water (10 per cent.), 102 parts.....	} Yielding 46.20 parts of ammonium acetate.
Ammonia water, stronger (28 per cent.), 86.48 parts.....	
Ammonium carbonate, 81.40 parts.....	

DILUTED ACETIC ACID.

ACIDUM ACETICUM DILUTUM.

Acetic acid 17 parts.
 Distilled water 83 parts.
 Mix them.

Properties and tests.—Diluted acetic acid contains 6 per cent. of absolute acetic acid, and has the sp. gr. 1.0088. It corresponds, in properties, to acetic acid, and should respond to the same tests of purity.

This diluted acetic acid is one-third stronger than that of the U. S. P., 1870, which contained only 4.50 per cent. of absolute acetic acid.

To neutralize 24 Gm. of dilute acetic acid should require 24 C.c. of the volumetric solution of soda.

Saturating power.—100 parts of the official (U. S.) diluted acetic acid, containing 6 per cent. of $\text{HC}_2\text{H}_3\text{O}_2$, will saturate alkalies as follows:

Potassa (90 per cent.), 6.22 parts.....	}	Yielding 9.80 parts of potassium acetate.
Solution of potassa (5 per cent.) 112 parts.....		
Potassium carbonate (81 per cent.), 14.89 parts.....		
Potassium bicarbonate, 10 parts		
Soda (90 per cent.), 4.44 parts.....	}	Yielding 3.60 parts of sodium acetate.
Solution of soda (5 per cent.), 80 parts.....		
Sodium carbonate (96 per cent.), 14.89 parts.....		
Sodium bicarbonate (99 per cent.), 8.49 parts.....		
Ammonia water (10 per cent.), 17 parts	}	Yielding 7.70 parts of ammonium acetate.
Ammonia water, stronger (28 per cent.), 6.07 parts		
Ammonium carbonate, 5.23 parts		

GLACIAL ACETIC ACID.

ACIDUM ACETICUM GLACIALE.

Nearly or quite absolute acetic acid.

Description.—At or below 15°C . (59°F .) a crystalline solid; at higher temperatures a colorless liquid. When liquefied and as near as possible to 15°C . (59°F .) it has the sp. gr. 1.056—1.058. Its properties are similar to those of acetic acid, and it is similarly affected by reagents.

To neutralize 8 Gm. of glacial acetic acid should require not less than 49.5 C.c. of normal solution of sodium hydrate (corresponding to at least 99 per cent. of absolute acetic acid).

Notes.—Glacial acetic acid was not contained in the U. S. Pharmacopœia of 1870. At low temperatures it crystallizes into an ice-like mass, and when it only partially congeals it has the appearance of a supersaturated solution.

When glacial acetic acid is diluted with water its specific gravity increases with a simultaneous fall in temperature until the mixture contains about 77 to 80 per cent. of hydrogen acetate. Upon the further addition of water, however, the specific gravity decreases and the temperature of the mixture rises. An acetic acid of 47 per cent. strength has the same specific gravity as the official glacial acetic acid, which is more than twice as strong.

The corrosive nature of glacial acetic acid renders it necessary to be very cautious in handling it, especially in removing the stopper from a full bottle which has been standing in a warm place, as vapors of the acid are liable to issue from the bottle with a rush at the moment the stopper is removed.

Saturating power.—100 parts of the official (U. S.) glacial acetic acid, containing 99 per cent. of $\text{HC}_2\text{H}_3\text{O}_2$, will saturate alkalies as follows:

Potassa (90 per cent.), 102.66 parts	} Yielding 161.66 parts of potassium acetate.
Solution of potassa (5 per cent.), 1848.0 parts	
Potassium carbonate (81 per cent.), 140.55 parts	
Potassium bicarbonate, 165 parts	
Soda (90 per cent.), 73.32 parts	} Yielding 224.43 parts of sodium acetate.
Solution of soda (5 per cent.), 1320 parts	
Sodium carbonate (96 per cent.), 245.82 parts	
Sodium bicarbonate (99 per cent.), 140 parts	
Ammonia water (10 per cent.), 280.50 parts	} Yielding 127.05 parts of ammonium acetate.
Ammonia water, stronger (28 per cent.), 100.18 parts	
Ammonium carbonate, 86.35 parts	

COMMERCIAL ACETIC ACIDS.

The several grades of acetic acid generally sold by dealers frequently differ from the Pharmacopœial standards. The kind labeled "C.P." is often of 1.040 sp. gr.; and an acid labeled "U. S. P." may be of 1.047 sp. gr., which was the standard of 1870. The acid sold as "glacial" is, or has until recently, been most frequently of between 75 and 80 per cent. strength (Squibb), but sometimes of 95.50 per cent. The so-called "No. 8" acetic acid may be of various degrees of strength and purity. Originally it was an acid of 32 per cent., and the designation "No. 8" was derived from the English excise system, in which the meaning of the term appears to have been that 1 part of this acid when diluted would furnish 8 parts of vinegar containing 4 per cent. of acetic acid. At the present time, in this country, a No. 8 acetic acid is about 80 per cent. at best, and may be even below 25 per cent.

POTASSIUM ACETATE.

POTASSII ACETAS.



Acetic acid	500 C.c.
Potassium bicarbonate	300 Gm.

Add the potassium bicarbonate gradually to the acid; filter; evaporate over a sand-bath to dryness, stirring constantly, adding a little acetic acid if necessary to keep it in decided excess to the end.

Must be kept in tightly corked bottles.

Reaction.— $\text{KHCO}_3 + \text{HC}_2\text{H}_3\text{O}_2 = \text{KC}_2\text{H}_3\text{O}_2 + \text{CO}_2 + \text{H}_2\text{O}.$

Notes.—Theoretically the proportions given in the foregoing formula leave the acetic acid slightly in excess; but this excess of acid will be driven off during the evaporation, and more must be added from time to time as may be required in order to maintain a slightly acid reaction.

The British Pharmacopœia directs the use of potassium carbonate, the proportions given being 20 avoirdupois ounces of the carbonate of potassium to 40 imperial fluidounces of the B. P. acetic acid, which is of 83 per cent. strength. The U. S. P. prefers potassium bicarbonate, which is more cheaply procured free from silicate and chloride.

The temperature during the evaporation should be 120° to 140° C. (248° to 284° F.).

Another method of preparation is as follows:

Lead acetate..... 13 parts.
Potassium bicarbonate..... 7 parts.

Dissolve each salt in about 40 parts of water, filter, and add the solution of lead acetate to that of the potassium bicarbonate, stirring well. Let settle. Decant the supernatant liquid which contains the potassium acetate, add enough acetic acid to it to render it slightly acid, and evaporate to dryness.

Collect and wash the precipitated lead carbonate.

Reaction.— $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 6\text{KHCO}_3 = 2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2 + 6\text{K}_2\text{C}_2\text{H}_3\text{O}_2 + 4\text{CO}_2 + 2\text{H}_2\text{O}$.

Description and tests.—A white deliquescent salt, which is soluble in alcohol, and which melts to an oily liquid above 275°C .

It is very soluble in water, and readily soluble in alcohol. Its aqueous solution should not be colored or precipitated by hydrogen sulphide, ammonium sulphide, ammonium carbonate, or barium chloride. Crystals dropped on strong sulphuric acid should impart no color, and with a dilute acid they should give no effervescence.

The absence of sodium acetate may be determined by the flame test or by evaporating 4.9 Gm. of the dry salt to complete dryness with pure hydrochloric acid. The residue of potassium chloride should weigh 3.72 Gm.

SODIUM ACETATE.

SODII ACETAS.

$\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O} = 136$.

Lead acetate..... 20 parts.
Sodium carbonate..... 15 parts.
Acetic acid, sufficient.

Dissolve the salts, each in sixty parts of water; filter, and add the solution of lead acetate to that of the sodium carbonate, stirring briskly. Set aside to settle. Decant the supernatant liquid; wash the precipitate with a little cold distilled water and add the washings to the decanted solution. Filter. Add enough acetic acid to the filtrate to render it distinctly acid to litmus paper; then evaporate it to 25 parts, and set it aside to cool and crystallize. Concentrate the mother liquor by evaporation, and crystallize again.

Must be kept in tightly corked bottles.

Reaction.— $3(\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}) + 3(\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}) = 2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2 + 6(\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}) + 20\text{H}_2\text{O} + \text{CO}_2$.

By-product.—The precipitated lead carbonate should be further washed until the washings cease to give an alkaline reaction to test-paper, and should then be dried.

Notes.—Another method consists in neutralizing acetic acid with sodium bicarbonate.

The salt effloresces on exposure, and in order to safely dry the crystals it is important that the temperature should not exceed 30° C. (86° F.). Still better is it to dry the crystallized salt in a strong current of cold air produced by a blower.

Description.—Colorless crystals, somewhat efflorescent in dry air, readily soluble in water, and soluble in alcohol. The aqueous solution should not be colored or precipitated by the reagents mentioned under Potassium Acetate.

SOLUTION OF ACETATE OF AMMONIUM.

LIQUOR AMMONII ACETATIS.

Diluted acetic acid 100 C.c.

Carbonate of ammonium, sufficient.

Add a sufficient quantity of carbonate of ammonium gradually to the diluted acetic acid, until the latter is neutralized.

This preparation should be freshly made, when required for use.

About 5 Gm. of ammonium carbonate is required.

Reaction.— $\text{NH}_4\text{HCO}_3 + \text{NH}_4\text{NH}_2\text{CO}_2 + 3\text{HC}_2\text{H}_3\text{O}_2 = 3\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 + 2\text{CO}_2 + \text{H}_2\text{O}.$

Notes.—To make a preparation such as the Pharmacopœia intends, the diluted acid should be cold in order that the free carbonic acid which is formed may dissolve in sufficient quantity in the liquid. The presence of this carbonic acid renders it impracticable to determine the exact point of neutralization by means of test-paper; but the taste is generally sufficiently reliable. The solution should have a pure saline taste, or the saline taste modified only by that of the carbonic acid; a slight excess of acetic acid is less objectionable than any excess of alkali. Even when neutral the solution gives an acid reaction to litmus paper owing to the carbonic acid.

When the ammonium carbonate dissolves in the acetic acid the temperature is lowered, on account of the liberation of carbonic acid gas. This fall of the temperature of the liquid is advantageous, as it aids the solution of another portion of the gas.

In some Pharmacopœias ammonia water is used instead of ammonium carbonate. In this case the temperature rises. Test-paper can be used to ascertain the reaction when this method is followed, but it is generally directed that the solution shall be, not neutral, but slightly acid. The alternate process of the Pharmacopœia consists in mixing equal quantities by weight of two solutions; one consisting of 10 parts of ammonium carbonate dissolved in 80 parts of distilled water, and the other of 28 parts of acetic acid in 62 parts of distilled water.

Reducing this formula to volumetric proportions for the sake of greater convenience, 10 Gm. of ammonium carbonate may be dissolved in a sufficient quantity of distilled water to make the solution measure 90 C.c., and 27 C.c. of acetic acid diluted with distilled water to measure 90 C.c. Equal volumes of these liquids will produce the official solution of ammonium acetate.

Description.—A clear, colorless liquid, completely volatile by heat. It should not be colored or precipitated by the reagents mentioned under the head of Potassium Acetate.

MAGNESIUM ACETATE.

MAGNESII ACETAS.

$\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 = 142.$

Magnesium carbonate 40 parts.

Acetic acid 137 parts.

Dissolve, filter, and evaporate to dryness.

A white, gummy, deliquescent salt, freely soluble in water and in alcohol.

ZINC ACETATE.

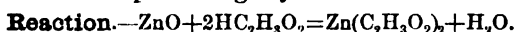
ZINCI ACETAS.



Zinc oxide.....	300 Gm.
Acetic acid.....	1,000 C.c.
Distilled water.....	1,000 C.c.

Mix 600 C.c. of the acid with the whole of the water in a flask, add the zinc oxide, agitate gently, and warm the mixture to about 60° C. (140° F.); add the remainder of the acid gradually, continuing the digestion until no more of the oxide is dissolved. Heat the solution to the boiling point; filter while hot, add a little acetic acid (about 10 C.c.) to insure that the acid is present in slight excess. Set the solution in a cool place for two days to crystallize. Decant the mother liquor, evaporate it over a water-bath to one-half, acidulate with acetic acid as before, if necessary, and again set aside to crystallize in a cool place. Put the crystals in a funnel to drain; then dry them on filter paper or on a porous tile, without the aid of heat.

Must be kept in a tightly corked bottle.

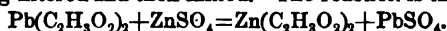


Notes.—The same result will be obtained if 420 Gm. of zinc carbonate be used instead of 300 Gm. of the oxide. The carbonate should be added gradually on account of the effervescence caused by the liberation of carbonic acid, and the solution formed is then to be boiled a few minutes to expel the carbonic acid perfectly.

When the preparation is made on a manufacturing scale from commercial zinc oxide or carbonate, it is necessary to digest the solution of acetate of zinc for several days with some pure metallic zinc, or with pure zinc oxide, in order to remove any lead, copper, cadmium and iron that may be present. By this digestion, however, some basic zinc acetate is formed, which must be converted into normal acetate by the addition of more acetic acid before crystallizing. A solution of basic salt will not crystallize, but the presence of a little free acetic acid facilitates the crystallization.

When the first crop of crystals has been collected, the mother liquor must be evaporated at a temperature not above 80° C. (176° F.) until a pellicle forms, after which it is set aside in a cool place. If the evaporation is carried too far a precipitate of zinc acetate containing but one molecule of water of crystallization will deposit.

Zinc acetate may also be made by double decomposition from 88 parts of lead acetate and 29 parts of zinc sulphate, each dissolved in 80 parts of distilled water, the solutions being filtered and then mixed. The reaction is then:



Description.—Soft, pearly white crystalline plates, with slight odor of acetic acid and sharp taste. Freely soluble in water, less soluble in alcohol.

Tests.—The aqueous solution must not be precipitated by barium chloride or silver nitrate, but should yield a pure white precipitate with hydrogen sulphide or ammonium sulphide, insoluble in acetic acid, but soluble in dilute mineral acids.

A pure white precipitate is produced by potassium hydrate, soluble in excess.

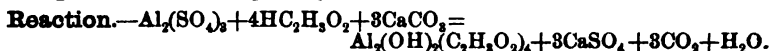
SOLUTION OF ALUMINIUM ACETATE.

LIQUOR ALUMINII ACETATIS; G.

Containing seven and one-half to eight per cent. of basic aluminium acetate ($\text{Al}_2(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)_4$, 324.)

Aluminium sulphate.....	30 parts.
Acetic acid	30 parts.
Precipitated calcium carbonate	13 parts.
Water	100 parts.

Dissolve the aluminium sulphate in 80 parts of water, and add the acetic acid. Mix the calcium carbonate with 20 parts of water, and add this mixture gradually and with constant stirring to the solution of aluminium sulphate. Set aside for twenty-four hours in a warm place, agitating the mixture frequently; then decant, and filter.



As will be seen by this equation, the solution must contain a small quantity of calcium sulphate, which is not insoluble in the liquid; and in mixing the calcium carbonate with the acid and aluminium sulphate, carbonic acid is evolved.

SOLUTION OF FERRIC ACETATE.

LIQUOR FERRI ACETATIS.

An aqueous solution of ferric acetate ($\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6$, 466) containing 33 per cent. of the anhydrous salt.

Solution of tersulphate of iron	100 parts.
Glacial acetic acid.....	26 parts.
Water of ammonia.....	80 parts.
Distilled water, sufficient.	

To the water of ammonia diluted with 200 parts of cold water add, constantly stirring, the solution of tersulphate of iron previously diluted with 350 parts of cold water. Pour the whole on a wet muslin strainer, allow the precipitate to drain, then return it to the vessel and mix it intimately with 600 parts of cold water; again drain it on the strainer,

and repeat the operation until the washings cause but a slight cloudiness with test solution of chloride of barium. Then allow the excess of water to drain off and press the precipitate, folded in the strainer, until its weight is reduced to 70 parts or less. Add the precipitate to the glacial acetic acid contained in a capacious porcelain capsule, and stir occasionally, until the hydrate is entirely dissolved. Finally, add sufficient cold distilled water to make the product weigh 100 parts, and filter if necessary.

Solution of acetate of iron should be kept in well stoppered bottles, protected from light.

Reaction.—First, $\text{Fe}(\text{SO}_4)_3 + 6\text{NH}_4\text{OH} = \text{Fe}_3(\text{OH})_8 + 3(\text{NH}_4)_2\text{SO}_4$; then $\text{Fe}_3(\text{OH})_8 + 6\text{HC}_2\text{H}_3\text{O}_2 = \text{Fe}_3(\text{C}_2\text{H}_3\text{O}_2)_8 + 6\text{H}_2\text{O}$.

Notes.—In order to make this preparation successfully, the directions of the Pharmacopœia must be strictly obeyed. Cold liquids must be used throughout, and if practicable the solution should be made in cool weather. See the notes on ferric hydrate. When the hydrate has been well washed and drained, as much as possible of the water held by the magma must be forcibly pressed out, and the weight of the hydrate thus reduced to the quantity stated. This is necessary because a larger quantity of moisture retained in the magma would so dilute the acetic acid that it could no longer dissolve the hydrate, so that a turbid mixture instead of a clear solution would result. No heat must be employed, because heat decomposes the ferric hydrate, depriving it of water of hydration and thus rendering it insoluble, whilst it at the same time volatilizes acetic acid. Even the elevation of temperature caused by the solution of the ferric hydrate in the strong acetic acid is too great not to be kept under control so far as practicable. To obviate this generation of heat, the ferric hydrate should be added in small portions at a time to the acid.

Filtration is impracticable, or perhaps worse than useless. If the solution is unclear, it will be rendered more so by any exposure to the air during filtration, from loss of acetic acid, and chemical changes, and even if the filtration be carried out so carefully as to effectually prevent loss of acid and access of air, the liquid will pass through the filter paper extremely slowly and rarely clearer than before.

The preparation is used in making the tincture.

Description.—A deep reddish brown liquid, with slight acid reaction and styptic taste.

It gives a red precipitate with ammonia water, and a blue with potassium ferrocyanide. Its sp. gr. is 1.160, and its sp. vol. 0.862.

TINCTURE OF ACETATE OF IRON.

TINCTURA FERRI ACETATIS.

Solution of ferric acetate	86 C.c.
Acetic ether	45 C.c.
Alcohol	74 C.c.

Mix the alcohol and acetic ether; then add the solution of ferric acetate slowly and in small quantities at a time.

Notes.—If the ferric acetate is added all at once, heat is generated, whereby acetic acid and acetic ether are volatilized, and the preparation is liable to become unclear from basic ferric acetate.

Must be kept in a well stoppered bottle in a cool dark place.

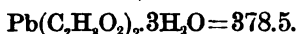
MIXTURE OF ACETATE OF IRON AND AMMONIUM.**MISTURA FERRI ET AMMONII ACETATIS.**

Tincture of chloride of iron	2 Gm.
Diluted acetic acid.....	3 Gm.
Solution of acetate of ammonium.....	20 Gm.
Elixir of orange	10 Gm.
Syrup.....	15 Gm.
Water	50 Gm.

To the solution of acetate of ammonium, previously mixed with the diluted acetic acid, add the tincture of chloride of iron, and then the elixir of orange, syrup and water, and mix the whole thoroughly.

Notes.—The preparation contains ferric acetate and ammonium chloride formed by double decomposition between the ferric chloride and ammonium acetate. Volumetrically the mixture consists of:

Tincture of ferric chloride.....	10 C.c.
Diluted acetic acid.....	15 C.c.
Solution of ammonium acetate.....	100 C.c.
Elixir of orange.....	45 C.c.
Syrup.....	55 C.c.
Water.....	250 C.c.

LEAD ACETATE.**PLUMBI ACETAS.**

Commercial "sugar of lead" is prepared from litharge and wood vinegar, and is purified by recrystallization if necessary. For pharmaceutical uses it is made by one of the following two processes:

FIRST METHOD.

Sugar of lead	30 parts.
Acetic acid	1 part.
Boiling distilled water.....	30 parts.

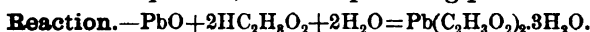
Dissolve, filter, and set aside to crystallize. Collect the crystals. Evaporate the mother liquor to one-half and set aside to crystallize again. Repeat the evaporation and crystallization of the mother liquor so long as a pure salt crystallizes, or as often as it proves profitable. Dry the crystals as rapidly as practicable, and without the aid of heat.

SECOND METHOD.

Oxide of lead, in fine powder	180 Gm.
Acetic acid.....	280 C.c.
Water	140 C.c.

Mix the acid and water, and dissolve the oxide in the mixture with the aid of a little heat. Filter, evaporate until a pellicle forms, and then set aside to cool and crystallize, adding first a little more acetic acid, if necessary, to give the solution a distinctly acid reaction.

Collect, drain, and dry the crystals, and evaporate the mother liquor to recover more product, as in the preceding process.



Notes.—If the concentrated solution is constantly stirred in cooling, or shaken in a wide-mouthed bottle, a granulated product is obtained. If allowed to crystallize at perfect rest and slowly, from dilute solutions, large crystals may be obtained. A granulated preparation (in minute crystals) is preferable for pharmaceutical purposes. The crystals should be drained as rapidly as possible—on muslin if the quantity is large—and dried in an atmosphere of acetic acid produced by sprinkling a little of the acid about the drying salt. The product, if the quantity is not too large, may be most conveniently and safely dried by gently pressing it between blotting paper, changing the paper several times, and as soon as moist, until the salt is dry.

Moist lead acetate rapidly absorbs carbonic acid from the air, if exposed, and forms insoluble carbonate. The surface of the crystals becomes white when covered with carbonate.

The salt also easily loses water of crystallization.

Lead acetate must be kept in well closed bottles in a cool place.

Description.—Glassy prismatic crystals which, when pure, are readily soluble in water, giving a clear solution. A turbidity indicates usually carbonate, and should disappear on addition of a drop or two of acetic acid. The crystals should be readily soluble in alcohol.

The aqueous solution should be completely precipitated by hydrogen sulphide, giving black lead sulphide. The filtrate should not be precipitated by ammonia water, ammonium sulphide or carbonate.

SOLUTION OF SUBACETATE OF LEAD.

LIQUOR PLUMBI SUBACETATIS.

An aqueous liquid containing in solution about 25 per cent. of subacetate of lead.

Acetate of lead	17 parts.
Oxide of lead	12 parts.
Distilled water, sufficient.	

Dissolve the acetate of lead in 80 parts of boiling, distilled water, in a glass or porcelain vessel. Then add the oxide of lead and boil for half an hour, occasionally adding enough hot distilled water to make up the loss by evaporation. Remove the heat, allow the liquid to cool, and add enough distilled water, previously boiled and cooled, to make the product weigh 100 parts. Finally, filter the liquid in a well covered funnel.

Solution of subacetate of lead should be kept in well stoppered bottles.

Reaction.— $\text{PbO} + \text{H}_2\text{O} + \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 = \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Pb}(\text{OH})_2$.

Notes.—At least four basic lead acetates are known, differing from each other in the percentage of acetic acid and in their solubility in water. They may all be prepared by the same method, the only difference being in the amount of lead oxide dissolved. In the preparations of the U. S. and British Pharmacopœias the di-basic lead acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Pb}(\text{OH})_2$) is probably the salt that is present in the greatest proportion; but some of each of the other basic acetates is also contained in the solution.

All of the oxide of lead added does not dissolve, no matter what may be the quantity, for a portion of it becomes converted into carbonate. As soon as the residue becomes quite white, no more of it will be dissolved.

Bottles containing solution of subacetate of lead soon become coated with lead carbonate, which forms a white crust on their sides. This white crust is most readily removed by nitric acid.

The preparation becomes whitish on dilution with water containing carbonic acid, sulphates, etc., and can be diluted so as to form a clear liquid only with distilled water.

Description.—A colorless solution with a sweetish taste and alkaline reaction. Sp. gr. about 1.228, and the sp. vol. accordingly about 0.814.

Uses.—It is employed in several other preparations, and frequently as a reagent in proximate analysis.

GLYCERITE OF SUBACETATE OF LEAD.

GLYCERITUM PLUMBI SUBACETATIS.

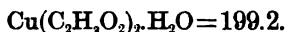
Lead acetate	250 Gm.
Lead oxide, in fine powder	175 Gm.
Glycerin	1,000 Gm.
Distilled water	600 C.c.

Mix in a porcelain dish and boil the mixture fifteen minutes. Filter and evaporate the filtrate to 1,000 C.c.

Notes.—This solution will bear dilution with distilled water, yielding a clear liquid. It has the same strength as the official solution of subacetate of lead.

COPPER ACETATE.

CUPRI ACETAS.



Subacetate of copper	100 Gm.
Diluted acetic acid	400 C.c.
Water	200 C.c.

Triturate the verdigris with enough water to form a smooth, thin paste. Then add the acid, mix well, transfer the mixture to a porcelain capsule, and heat it over a water-bath at not over 80° C. (176° F.) until solution is effected. Filter while hot. Set aside to cool and crystallize. Collect and dry the crystals on blotting paper in a cool place.

Reaction.— $\text{Cu}_2\text{O} \cdot (\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} = 2(\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O})$.

Notes.—To obtain good crystals a slight excess of acetic acid must be present during the evaporation and crystallization. Should the liquid become unclear from blue di-basic copper acetate, through loss of acetic acid by evaporation, more acid must be added.

Additional crops of crystals can be obtained from the mother liquor on evaporation.

The total product should be at least equal to the weight of the verdigris used. The crystals should be distinct, deep green, and should make perfectly clear solutions with water, or with ammonia water.

Must be kept in a well corked bottle, and in a cool place.

Another method is as follows:

Copper sulphate.....	2 parts.
Lead acetate.....	3 parts.
Acetic acid, sufficient.	

Dissolve each salt separately in 6 parts of water. If necessary add a little acetic acid to the solution of the lead acetate to render it clear. Filter the solutions. Mix them. Filter. Collect the filtrate containing the copper acetate, evaporate it on a water-bath at not over 80°C . (170°F .) until a pellicle begins to form, taking care to keep acetic acid present in excess. Then set aside to crystallize.

Reaction.— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O} =$
 $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O} + \text{PbSO}_4 + 7\text{H}_2\text{O}$.

Notes.—Handsome rhombic crystals of normal cupric acetate with 5 molecules of water are formed if a solution saturated at 60°C (140°F .) is rapidly cooled; when warmed to about 80°C . (166°F .) these crystals lose 4 molecules of water and turn green and opaque, but retain their form.

Copper acetate readily loses acetic acid and water, becoming basic, insoluble, and blue or light green. Hence the necessity of keeping the salt in a tightly closed bottle in a cool place.

In the process of preparation it should not be exposed to the air and to heat any more than is unavoidable.

Description.—Dark green crystals with metallic taste and acetous odor. Completely soluble in water, and difficultly soluble in alcohol. They effloresce on exposure to the air.

VALERATES.

The sodium and ammonium valerates are readily soluble in water, and are prepared by neutralizing the acid with the carbonates or hydrates. Zinc valerate is not readily soluble, and ferric valerate is insoluble; these two are made from the sodium salt by double decomposition.

VALERIC ACID.

ACIDUM VALERIANICUM.



This acid exists in valerian, anthemis, angelica, old hops, etc. It is also obtained by the oxidation of certain organic substances, and is now

prepared mainly by oxidizing amylic alcohol with chromic acid, as described under the title, Sodium Valerate. From this salt the acid is obtained by adding sulphuric acid, when the oily valeric acid rises to the surface, and is separated and distilled after having been deprived of water by shaking it repeatedly with strong sulphuric acid.

Description.—A thin, oily liquid, with a peculiar sharp disagreeable odor, which is very characteristic. It does not mix in all proportions with water, but requires between 26 and 30 parts by weight for solution.

It dissolves in all proportions in alcohol and ether. It boils at 175° C., and has a specific gravity of .9536 at 0° C.

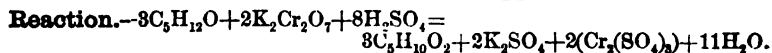
SODIUM VALERATE.

SODII VALERIANAS.



Amylic alcohol	800 C.c.
Potassium bichromate	1,800 Gm.
Sulphuric acid	1,300 C.c.
Water	16,000 C.c.
Solution of soda, sufficient.	

Dilute the sulphuric acid with 2,000 C.c. of the water. Dissolve the potassium bichromate in the remainder of the water with the aid of heat. When both liquids are cold mix them with the amylic alcohol in a retort or flask, with occasional brisk agitation, until the temperature of the mixture has fallen to about 32° C. (89.° 6 F.). Connect with a condenser, and distil until about 16,000 C.c. of distillate has been obtained. Saturate the distilled liquid accurately with the solution of soda, remove any oily fluid which floats on the surface, evaporate until watery vapor ceases to escape, and then raise the heat cautiously until the salt is liquefied. When the product has cooled and solidified, break it into pieces, and immediately put it into a stoppered bottle.



Notes.—The bichromate of potassium is decomposed by the sulphuric acid, the products being potassium sulphate and chromic acid. The amylic alcohol is then oxidized by the chromic acid, and when the mixture is subjected to distillation, the distillate consists of valeric acid and amyl valerate (or apple oil).

When sodium hydrate is added to the liquid, the amyl valerate separates as an oily layer, whilst the valeric acid is neutralized, forming sodium valerate. If the oily amyl valerate be warmed with the soda solution it is decomposed, yielding sodium valerate and amylic alcohol, which also appears as an oily liquid on the surface of the solution. After removing the oily fluid, the solution of sodium valerate is evaporated and the salt fused.

Description.—White crystals, soluble in water and alcohol. The crystals absorb water from moist air, and liquefy. They melt without decomposition, at a temperature of 140°. The aqueous solution should remain colorless when treated with hydrogen sulphide or ammonium sulphide.

AMMONIUM VALERATE.**AMMONII VALERIANAS.**

Prepared by saturating valeric acid with dry ammonia gas, usually generated from a mixture of equal parts of ammonium chloride and lime. The heat produced by the chemical union keeps the salt in a liquid condition, and on cooling the valerate crystallizes. The salt cannot be crystallized from an aqueous solution.

A solution of ammonium valerate may be readily prepared by dissolving 102 Gm. of valeric acid in 61 Gm. of stronger water of ammonia; if diluted with distilled water until it measures 238 cubic-centimeters, each C.c. of this solution will contain 0.50 Gm. of the salt.

Neutral ammonium valerate easily parts with ammonia and becomes acid; in solution it is to be carefully neutralized with ammonia water.

Description.—Colorless crystalline plates, soluble in water and alcohol, and having odor of the acid. They should volatilize completely.

ZINC VALERATE.**ZINCI VALERIANAS.**

Sodium valerate	25 parts.
Zinc sulphate	29 parts.
Distilled water, sufficient.	

Dissolve the salts, separately, each in 200 parts of water; heat the solutions to boiling; mix while hot; let the mixture cool. Collect the crystals, wash them hastily with cold water, and dry them between filter-paper.

Another crop may be had by evaporating the mother liquor to 20 parts, cooling, and separating the crystals formed.

Reaction.— $2\text{NaC}_5\text{H}_9\text{O}_2 + \text{ZnSO}_4 = \text{Zn}(\text{C}_5\text{H}_9\text{O}_2)_2 + \text{Na}_2\text{SO}_4$.

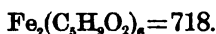
Notes.—As the zinc valerate is lighter than the solution of sodium sulphate, the crystals rise to the surface as they are formed.

The salt may also be made by dissolving 8 parts of zinc oxide in a mixture of 5 parts of valeric acid, 200 parts of alcohol, and 200 parts of water; but the crystallization is tedious on account of the necessity of using but moderate heat in evaporating the solution.

The crystals must be dried without the aid of heat.

Description.—Soft, glistening white crystals, soluble in about 100 parts of water, also soluble in excess of ammonia water.

The solution should give a perfectly white precipitate with hydrogen sulphide.

FERRIC VALERATE.**FERRI VALERIANAS.**

Prepared by adding a cold dilute solution of ferric chloride to a solution of sodium valerate so long as a precipitate is formed. The product is collected on a filter, washed with a little cold water, and dried without the aid of heat.



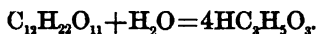
Description.—A reddish brown powder, insoluble in water. It is decomposed by boiling water, with liberation of valeric acid and ferric hydrate.

LACTATES.

Those of zinc and iron are alone used. Both are soluble in water, but require a large proportion of the solvent.

LACTIC ACID.**ACIDUM LACTICUM.**

Milk-sugar yields, by fermentation, lactic acid:



Several other organic substances, as dextrin, glucose, etc., are also capable of undergoing lactic fermentation.

When a mixture of 100 parts of sugar dissolved in sufficient water to yield a solution of about 1.06 sp. gr., with 8 to 10 parts of old cheese, and 50 parts of prepared chalk, is exposed for several weeks to a moderate heat, such as is afforded in a sunny place in the summer, calcium lactate is formed which is found crystallized in the liquid. The lactate of calcium is recrystallized, if necessary, and decomposed by sulphuric acid, yielding lactic acid and calcium sulphate.

Lactic acid is also prepared from milk-sugar and skimmed milk, a mixture of 300 Gm. of milk-sugar and 4,000 C.c. of milk being exposed

to a temperature of 20° to 30° C. (68° to 86° F.), and the acid neutralized from time to time with sodium bicarbonate, until the lactic fermentation ceases. The solution of lactate of sodium is then evaporated to a syrupy consistence, dissolved in alcohol, and decomposed by sulphuric acid, after which the lactic acid is neutralized with chalk, and the lactate of calcium in turn decomposed to obtain a purer product. (See also, Ferrous Lactate).

Description.—A colorless, or very pale yellowish, syrupy liquid, odorless or nearly so, acid to the taste. Sp. gr. 1.212; sp. vol. 0.835. Miscible in all proportions with water, alcohol, and ether, but nearly insoluble in chloroform.

Tests.—Warmed with potassium permanganate it develops an odor of aldehyde. When heated it vaporizes, and decomposes at about 176° C. (350° F.) yielding inflammable gases, which at first burn with a blue flame.

A solution of lactic acid in ten parts of water, neutralized with ammonia, is not precipitated by ammonium sulphhydrate. Not more than a faint opalescence is caused by barium chloride, silver nitrate, or ammonium oxalate; no precipitate is formed when it is boiled with an excess of Fehling's solution.

To neutralize 4.50 Gm. of the acid should require 37.50 C c. of the normal solution of sodium hydrate, indicating 75 per cent. of $\text{HC}_3\text{H}_5\text{O}_3$.

Saturating power.—100 parts of the official (U. S.) lactic acid, containing 75 per cent. of $\text{HC}_3\text{H}_5\text{O}_3$, will saturate:

Potassium bicarbonate, 88.83 parts	}	Yielding 106.67 parts of potassium lactate.
Sodium bicarbonate, 70 parts.....		
Sodium carbonate, 119.1 parts.....	}	Yielding 93.33 parts of sodium lactate.
Ammonium carbonate, 43.52 parts.....		
Ammonia water (10 per cent.), 141.17 parts....	}	Yielding 89.17 parts of ammonium lactate.
Ammonia water, stronger (28 per cent.), 50.60 parts.....		

ZINC LACTATE.

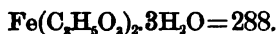
ZINCI LACTAS.



Prepared by neutralizing warm dilute lactic acid with zinc carbonate, and crystallizing.

Can also be prepared by double decomposition between sodium lactate and zinc chloride.

White or colorless quadrangular crystals, inodorous, and having an acidulous metallic taste, and acid reaction. Soluble in 58 parts of cold and 6 parts of boiling water; nearly insoluble in alcohol. Heated to 100° C. (212° F.) it loses its water of crystallization.

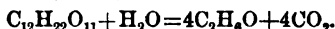
FERROUS LACTATE.**FERRI LACTAS.**

Dissolve 12 parts of powdered milk-sugar in 240 parts of whey from spontaneously soured milk; let the solution stand in a place where the temperature is maintained at from 30° to 50° C. (86° to 95° F.), and, after fermentation has commenced, neutralize the liquid daily with sodium bicarbonate until about 13 to 14 parts of the bicarbonate have been used. Heat the liquid to the boiling point, add dilute sulphuric acid until an acid reaction is produced; filter, and evaporate the filtrate over a water-bath until reduced to one-sixth of its weight. To the hot liquid add a solution of 9 parts of ferrous sulphate in 18 parts of hot distilled water. Strain or filter the solution, and set it aside for several days to crystallize. Collect the crystals, wash them with a little cold distilled water, and afterwards with a little alcohol; press them gently between filter paper, and dry the product with the aid of gentle heat.

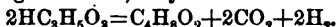
Must be kept in tightly closed bottles, in a cool, dry place.

Notes.—The whey contains 4 to 5 per cent. of milk-sugar, and this, together with that added, yields lactic acid, as shown above.

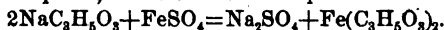
Unless this acid is neutralized from time to time, the lactic fermentation, which ordinarily continues for a week, may change to vinous and acetic fermentation. The production of alcohol and acetic acid might also follow if the temperature of the liquid is below 20° C. (68° F.):



Should the temperature be allowed to exceed 40° C. (104° F.), or an insufficient quantity of milk-sugar be used, butyric acid will be formed:



To arrest further fermentation, the liquid is heated to the boiling point, which at the same time coagulates, and facilitates the removal of albuminoid matters. Dilute sulphuric acid is added to prevent the formation of ferric salt, throwing down ferric hydrate, which is filtered out, and to decompose any alkali which may have been added in excess. The solution of sodium lactate is then mixed with solution of ferrous sulphate, when double decomposition results:



The crystals of ferrous lactate are removed from the mother liquor, and then rinsed free from sodium sulphate by cold water, after which the water adhering to the salt is washed off with a little alcohol to facilitate subsequent drying. The product must be dried at not above 30° to 40° C. (86° to 104° F.) as rapidly as practicable to prevent oxidation.

If not thoroughly dry when put up it soon oxidizes.

Description.—Yellowish green crystalline masses, or a greenish white powder, nearly inodorous, having a sweetish ferruginous taste, and a slightly acid reaction. Soluble in 40 parts of water at 15° C. (59° F.), and in 12 parts of boiling water. Freely soluble with a green color in solutions of alkali citrates. Nearly insoluble in alcohol.

Tests.—A preparation entirely free from ferric lactate cannot be produced. The less ferric salt the preparation contains, the greener will be its color. It should have the proper greenish color, and yield a greenish solution with water. As the solution of this salt in water is always a slow process, the ferrous lactate should be triturated to fine powder before adding the water. The filtered solution should not be rendered turbid by solution of lead acetate (sulphates, chlorides, tartrates, citrates, malates, etc.).

CHAPTER XXIII.

OLEATES.

Soaps and lead plaster are the most familiar oleates.

Soft soap is chiefly potassium oleate with some stearate and palmitate, and hard soap contains sodium combined in the same way. Other soaps are mixtures of potassium and sodium oleate.

The alkali oleates are soluble in water, are detergent, and are the *soaps proper*. The insoluble oleates of the earth metals and heavy metals are called *plasters*.

The "soap" official in the U. S. P. is sodium oleate prepared by boiling olive oil with caustic soda; the "green soap" of the Pharmacopœia is chiefly potassium oleate, prepared by boiling animal or vegetable oils with caustic potassa.

OLEIC ACID.

ACIDUM OLEICUM.



Impure oleic acid, known as "red oil," is obtained as a by-product in the manufacture of candles. Fats consist of olein, palmitin and stearin, which are the glycerides of oleic, palmitic and stearic acids.

The solid fatty acids (palmitic and stearic acids) are separated for use in making candles, and the residue, called "red oil," is crude oleic acid.

This red oil is purified by exposing it to a temperature of about $4^{\circ}.5$ C. (40° F.) when the stearic and palmitic acids contained in it solidify and are removed by pressing and straining, after which the crude acid is treated with sulphurous acid, washed, and filtered.

The product is far from being chemically pure, but is sufficiently pure for pharmaceutical and medicinal uses.

Description.—A pale yellow, or light sherry-colored, nearly inodorous and tasteless, oily liquid, of neutral or but faintly acid reaction. Exposed to the air it darkens, becoming brown, and assumes a decidedly acid reaction. Sp. gr. 0.860 to 0.890. Insoluble in water but readily soluble in alcohol, chloroform and ether.

Tests.—It forms a nearly colorless or but slightly yellowish potash soap, 80 parts being completely saponified by 8 parts of potassium carbonate dissolved in twice its weight of water, and the saponification aided by gentle heat.

POTASSIUM OLEATE.

POTASSII OLEATUM.



A good green soap for pharmaceutical purposes can be made by boiling together 40 parts of flaxseed oil, 2 parts of soda, 8 parts of potassa, and 40 parts of water. The product will contain some free alkali and the glycerin formed by the saponification. The small amount of soda added renders the soap less thin and smeary.

Solution of potassium oleate for making mercuric oleate is prepared as follows:

Potassium bicarbonate	75 Gm.
Oleic acid	210 Gm.

Add the potassium carbonate gradually to 3,000 C.c. of boiling water. When effervescence has ceased and the bicarbonate has been converted into normal carbonate of potassium, add the oleic acid, stir well, and continue heating the mixture gently, adding more water if necessary, until saponification is complete. Then dilute the solution with enough water to make it measure 4 liters.

Each liter of this solution represents 60 Gm. of potassium oleate.

SODIUM OLEATE.**SODII OLEATUM.**

To saponify 100 parts of fat requires about 14 parts of sodium hydrate. The best grades of white castile soap approach pure sodium oleate sufficiently for all practical purposes in pharmacy. Other oleates are conveniently prepared by double decomposition from water-soluble metallic salts and a solution of castile soap. For this purpose Conti's brand of white castile soap, dried and powdered to avoid any considerable variation in the percentage of moisture, should be used.

A solution of sodium oleate may be made by stirring the powdered soap with four times its weight of water until a uniform transparent mixture results. Then twice as much more water is added, and the mixture heated until solution takes place, yielding a slightly turbid liquid when cooled, after which it may be diluted to the desired point. For preparing oleates by double decomposition, a solution containing one avoirdupois ounce in each wine pint has been found to work well

AMMONIUM OLEATE.**AMMONII OLEATUM.**

The ammonia liniment of the Pharmacopœia is an imperfect soap formed by shaking together 12 parts of water of ammonia and 28 parts of cotton seed oil. Although a white emulsion-like mixture is at once obtained, the compounds formed are not permanent. Gradual changes take place, and the so called "liniment" becomes thicker and finally yellowish. When the proportions are changed to 12 parts of ammonia water and 40 parts of cotton seed oil, the product has a more uniform creamy consistence, containing in that case much more uncombined oil, which prevents the thickening of the liniment. Whatever the proportions may be, all the oil used should be added at once in order to insure a uniform liniment.

CALCIUM OLEATE.**CALCII OLEATUM.**

Lime soap is formed in the preparation of "lime liniment," which consists of equal parts of lime-water and cotton seed oil well shaken

together, all of the oil being added to the lime-water at once. An imperfect saponification takes place. The liniment is a creamy, light yellowish mixture.

ZINC OLEATE.

ZINCI OLEATUM.



Zinc acetate 60 Gm.
White castile soap, in powder 150 Gm.

Dissolve the acetate in 4,000 C.c. of cold water, and the soap in 2,000 C.c. of hot water. Add the solution of sodium oleate, when cold, to the solution of zinc acetate, stirring briskly. Drain the precipitated zinc oleate on a muslin strainer, and wash it several times with cold water. Dry it on paper or muslin, protecting it well from dust, and without the aid of heat.

Reaction.— $2\text{NaC}_2\text{H}_3\text{O}_2 + \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 = \text{Zn}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2 + 2\text{NaC}_2\text{H}_3\text{O}_2$.

Notes.—Zinc sulphate cannot be used as advantageously as the acetate for preparing zinc oleate, because the sodium sulphate is difficult to wash out from the pulverulent precipitate. The yield is about 70 Gm. or more, and the product contains 12.90 per cent. of zinc oxide.

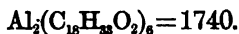
Description.—A soft, white powder, having a soapy feel.

Other zinc oleates, containing 5 or 10 per cent. of oxide, are made by dissolving oxide of zinc in oleic acid. The oxide is triturated with the acid in a mortar until they are well mixed; the mixture is set aside for two hours, and is afterwards heated gently over a water-bath until perfect solution has been effected. A soft, white, homogeneous ointment is formed.

The oxide used should be free from iron; otherwise the product will have a reddish or yellowish tint.

ALUMINIUM OLEATE.

ALUMINII OLEATUM.



Potassa alum 60 Gm.
White castile soap, in fine powder 110 Gm.

Dissolve the alum in 3,600 C.c. of water, and the soap in 1,800 C.c. of hot water. Pour the cold soap solution gradually into the alum

solution. Warm the mixture until the oleate separates. Decant the mother liquor, wash the oleate twice with hot water, using 3,000 C.c. of water each time, and then collect the product.

Reaction. — $6\text{NaC}_{18}\text{H}_{35}\text{O}_2 + \text{K}_2\text{Al}_2(\text{SO}_4)_4 = \text{Al}_2(\text{C}_{18}\text{H}_{35}\text{O}_2)_6 + \text{K}_2\text{SO}_4 + 3\text{Na}_2\text{SO}_4$.

Notes.—To free this oleate from water it must be melted in an evaporating dish by very gentle heat over the water-bath.

The yield is about 100 Gm. or slightly over that amount.

Description.—Aluminium oleate is a soft, white plaster, containing 5.86 per cent. of aluminium oxide.

FERRIC OLEATE.

FERRI OLEATUM.



Solution of normal ferric sulphate 90 C.c.

White castile soap, in fine powder 150 Gm.

Dilute the solution of ferric sulphate with 5,000 C.c. of water, and dissolve the soap in 2,500 C.c. of hot water. Mix the solutions. Wash the precipitated oleate twice with hot water, using about ten liters each time.

Reaction.— $\text{Fe}_2(\text{SO}_4)_3 + 6\text{NaC}_{18}\text{H}_{35}\text{O}_2 = \text{Fe}_2(\text{C}_{18}\text{H}_{35}\text{O}_2)_6 + 3\text{Na}_2\text{SO}_4$.

Notes.—The yield is about 120 Gm.

Ferrous oleate can also be made by double decomposition, from ferrous sulphate and soap, but the greenish ferrous oleate soon oxidizes.

Description.—Ferric oleate is a dark red, soft plaster.

LEAD OLEATE.

PLUMBI OLEATUM.



Lead acetate 100 Gm.

White castile soap, in fine powder 165 Gm.

Dissolve the lead acetate in ten liters of water; if decidedly milky, add to it, gradually, enough acetic acid to render the solution clear, being careful to avoid adding an excess of the acid. Dissolve the soap in 2,500 C.c. of hot water, and add this solution slowly to that of the lead acetate. Boil the mixture, reject the mother liquor, wash the precipitated oleate twice with boiling water, using ten liters each time. Separate the water from the product.



Notes.—Prepared in this manner the lead oleate is a hard, brittle, white plaster when cold. The yield is about 160 Gm. This lead oleate is more hard and brittle than lead plaster, which is made by boiling lead oxide with olive oil and water. It contains 28.95 per cent. of lead oxide. An oleate of lead containing 20 per cent. of lead oxide dissolved in an excess of oleic acid is readily obtained by digesting 4 parts of lead oxide in fine powder with 4 parts of oleic acid at about 60° C. (150° F.), stirring frequently until combined, the product being a soft yellowish ointment.

COPPER OLEATE.

CUPRI OLEATUM.



Copper sulphate..... 60 Gm.
White castile soap, in fine powder..... 150 Gm.

Dissolve the copper sulphate in five liters of water, and the soap in three liters of hot water. Pour the soap solution into that of the copper sulphate, stirring well. Wash the precipitated oleate twice, using ten liters of hot water each time. Collect the dark green oleate, squeeze the water out of it, and fuse it by very gentle heat, over the water-bath.



Notes.—The product is about 290 Gm., of a dark green, waxy plaster, containing 12.67 per cent. of copper oxide.

MERCURIC OLEATE.

HYDRARGYRI OLEATUM.



Yellow mercuric oxide..... 30 Gm.
Nitric acid (1.42 sp. gr.)..... 26 Gm.
Solution of potassium oleate..... 1,500 C.c.

Mix the oxide, the acid, and 200 C.c. of distilled water, in a beaker or an evaporating dish, and heat the mixture until the oxide dissolves, adding a few drops more of nitric acid, *if necessary*. Dilute the solution of mercuric nitrate thus formed with three liters of water. Add 1,500 C.c. of solution of potassium oleate (prepared as described under that title). Warm the mixture and wash the separated mercuric oleate twice

with warm distilled water, using about one liter each time. Subject the oleate to a low temperature in a mortar, and then press out of it all the water by means of a pestle.



Notes.—Yellow mercuric oxide is used in preference to red oxide of mercury because the latter is liable to contain a little nitrate. This, however, would not affect the result otherwise than to slightly diminish the total product, and to render the solution of mercuric nitrate more acid. Mercuric chloride cannot be employed in place of the nitrate, nor can sodium oleate be used instead of the potassium oleate, as the washing then becomes very difficult.

The yield is about 100 Gm. or a little more. The product is a soft, yellow or reddish yellow solid, and contains 28.4 per cent. of mercuric oxide.

The official "Oleate of Mercury" (U. S. P.), is a liquid, being a solution of 1 part of mercuric oxide in 9 parts of oleic acid. This oleate is best prepared at not over 40° C. (104° F.), the little lumps of oxide being carefully broken down by rubbing between two horn or wooden spatulas, two or three times a day, until the oxide is perfectly dissolved, which requires two or three days. An oleate containing 20 per cent. of oxide may be made in the same manner, using only 4 parts of oleic acid for each part of oxide; but the complete solution of the oxide will then require about a week or ten days.

Mercuric oleate is very sensitive to heat, decomposing with the separation of finely divided, dark colored, metallic mercury. Precipitated oleate of mercury containing no free oleic acid keeps better than solutions of mercuric oleate in free oleic acid, and the semi-solid "20 per cent. oleate" keeps better than the liquid "10 per cent. oleate" (containing 10 per cent. of oxide).

SILVER OLEATE.

ARGENTI OLEATUM.



Crystallized silver nitrate 25 Gm.

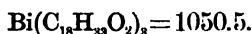
White castile soap, in fine powder 45 Gm.

Dissolve the silver nitrate in 1,500 C.c. of cold distilled water, and the soap in 500 C.c. of hot water. Add the soap solution very slowly and with brisk stirring to the silver solution. Collect the oleate, drain it, and wash it several times with cold distilled water. Dry it without the aid of heat, protecting it from exposure to light or dust.



Notes.—Silver oleate is very sensitive to light, heat, and contact with dust, impure air, etc. When first formed it is nearly white, but cannot be kept so unless it is prepared at night or in a dark room. Decomposition may be to a great extent prevented by surrounding and covering with yellow paper the funnel in which the oleate is washed. If properly precipitated it is finely granular, and it should be dried by the use of white blotting paper, frequently changed. If carefully protected the product will be of a light purplish white color.

The product is about 56 Gm., containing 29.77 per cent. of silver oxide. It should be kept in small amber glass stoppered bottles, wrapped in yellow paper.

BISMUTH OLEATE.**BISMUTHI OLEATUM.**

Normal bismuth nitrate 20 Gm.

White castile soap, in fine powder 32 Gm.

Put the crystals of normal nitrate of bismuth into a mortar, powder the salt, and then add, all at once, 100 C.c. of glycerin; stir occasionally, avoiding friction or pressure, until the nitrate is dissolved, which will be accomplished in a few hours. Dissolve the soap in 1,500 C.c. of water, and then add slowly the solution of nitrate of bismuth. Warm the mixture, reject the watery mother liquor, and wash the oleate twice with warm distilled water.



Notes.—The normal nitrate of bismuth is to be powdered before adding the glycerin, and the glycerin is added all at once to prevent possible explosion of nitroglycerin, which might be formed. This oleate must be fused by very gentle heat, over a water-bath, to get rid of the last portions of water. The yield is about 86 Gm., and the product is a white or yellowish white ointment containing about 22.22 per cent. of bismuthous oxide.

CHAPTER XXIV.**OXALATES.**

The oxalates are of little importance except the ammonium oxalate, which is used as a reagent for calcium salts, and for other purposes in analytical chemistry. Those of cerium and iron are insoluble; the oxalates of potassium and ammonium are soluble, and are prepared by neutralizing the acid with the carbonates or hydrates.

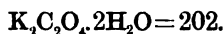
OXALIC ACID.**ACIDUM OXALICUM.**

Oxalic acid occurs in many plants in the form of oxalates of calcium and potassium. It is, however, manufactured by heating sugar, starch, gum, saw-dust, or other organic matters with nitric acid, or with alkali hydrates. The most common process of manufacture consists in heating a pasty mixture of saw-dust and solution of soda and potassa at $204^{\circ} \cdot 5$ C. (400° F.) for an hour or two. The dried mass contains 28 to 30 per cent. of oxalic acid as oxalates; by washing with sodium carbonate solution, the potassium oxalate is decomposed, leaving all of the oxalic acid in the form of sodium oxalate, the potassium carbonate being removed. The sodium oxalate is then treated with calcium hydrate, whereby calcium oxalate and sodium hydrate are produced. The calcium oxalate is then decomposed by sulphuric acid, and the oxalic acid purified by re-crystallization. The yield of oxalic acid equals about one-half of the weight of the saw-dust used.

Description.—Prisms, readily soluble in water and alcohol. It has a strong acid taste, and is a powerful poison in large doses. The crystals lose water over sulphuric acid, becoming anhydrous.

Heated alone or with strong sulphuric acid decomposition takes place, water, carbon monoxide and dioxide being formed.

Tests.—The crystals should be clear white, should be completely soluble in water, and should leave no residue on platinum when strongly heated. Addition of excess of ammonia water to the aqueous solution should not produce turbidity. The quantitative determination of oxalic acid with solution of potassium permanganate is given later.

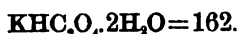
NORMAL POTASSIUM OXALATE.**POTASSII OXALAS.**

Oxalic acid.....	126 Gm.
Potassium bicarbonate.....	200 Gm.
Distilled water.....	1,000 C.c.

Dissolve the oxalic acid in the water by the aid of heat; then add the potassium bicarbonate. Neutralize perfectly. Evaporate and crystallize.

Reaction.— $2\text{KHCO}_3 + \text{H}_2\text{C}_2\text{O}_4 = \text{K}_2\text{C}_2\text{O}_4 + 2\text{CO}_2 + 2\text{H}_2\text{O}.$

Description.—Transparent prisms or pyramids, easily soluble in water.

ACID POTASSIUM OXALATE.**POTASSII BINOXALAS.**

Oxalic acid	126 Gm.
Potassium bicarbonate	100 Gm.
Distilled water	1,000 C.c.

Dissolve the potassium bicarbonate in the water by the aid of heat, boiling the liquid until effervescence ceases; then add the oxalic acid, dissolve, filter while hot, and set aside to cool and crystallize.

Reactions.— $2\text{KHCO}_3 = \text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$; then,
 $\text{K}_2\text{CO}_3 + 2\text{H}_2\text{C}_2\text{O}_4 = 2\text{KHC}_2\text{O}_4 + \text{CO}_2 + \text{H}_2\text{O}.$

Notes.—The acid potassium oxalate occurs naturally in several plant juices, as in sorrel, wood-sorrel, etc.

Description.—Occurs usually as anhydrous prisms or crystallized with one or two molecules of water. The salt unites with oxalic acid to form the quadroxalate.

It is not readily soluble in cold water.

AMMONIUM OXALATE.**AMMONII OXALAS.**

Oxalic acid	100 Gm.
Boiling distilled water	800 C.c.
Ammonium carbonate, sufficient.	

Dissolve the acid in the water, neutralize with ammonium carbonate, raising the temperature, at the end of the neutralization, to the boiling point; filter while hot, and set aside to cool and crystallize.

Reaction.— $2(\text{NH}_4\text{HCO}_3 \cdot \text{NH}_4\text{NH}_2\text{CO}_2) + 3\text{H}_2\text{C}_2\text{O}_4 =$
 $8(\text{NH}_4)_2\text{C}_2\text{O}_4 + 4\text{CO}_2 + 2\text{H}_2\text{O}.$

Notes.—About 120 Gm. of ammonium carbonate will be required. Instead of this 280 C.c. of ammonia water (10 per cent.) may be used. The solution should be rendered exactly neutral to test-paper, filtered while hot, and set aside to cool slowly. When the solution is dilute and the cooling and crystallization slow, very handsome needle-shaped crystals may be obtained. By evaporating the mother liquor and again crystallizing, additional crops of the salt are recovered.

Description.—This salt crystallizes in rhombic prisms, easily soluble in water without turbidity. The solid should volatilize completely on platinum.

CERIUM OXALATE.**CERII OXALAS.**

Silicate of cerium exists in the minerals cerite and allanite. From these minerals the cerium oxalate is prepared by a somewhat complicated process.

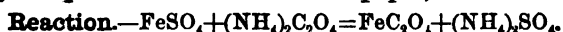
Description.—A white powder, tasteless and insoluble in water, but readily soluble in dilute acids.

Tests.—Should yield nothing to water, should not effervesce with acids. The solution in hydrochloric acid must not be colored by hydrogen sulphide.

FERROUS OXALATE.**FERRI OXALAS.**

Ferrous sulphate	200 Gm.
Oxalic acid	150 Gm.
Ammonia water	300 C.c.

Dissolve the oxalic acid in the ammonia water diluted with 2,000 C.c. of water; and the ferrous sulphate in 3,000 C.c. of hot water; filter the solutions, and then mix them. Wash the precipitate by decantation and afterwards on a filter until the washings are tasteless. Dry the product between bibulous paper, with the aid of gentle heat.



Notes.—Ferrous oxalate can also be made by the process official in the U. S. P. of 1870, which prescribed 2 troyounces of ferrous sulphate dissolved in 30 fluidounces of water to be added to a solution of 436 grains of oxalic acid in 15 fluidounces of water. When this process is followed ferrous oxalate and free sulphuric acid are formed, the precipitate separates slowly, and a considerable loss results from the fact that the oxalate is not insoluble in the sulphuric acid. Moreover, the proportions are incorrect, as 170 parts of ferrous sulphate require 126 parts of oxalic acid. By neutralizing nearly all of the oxalic acid with ammonia, using a slight excess of oxalic acid, and mixing the solution of ferrous sulphate with the acid solution of ammonium oxalate, the precipitate falls at once, and no loss of product is sustained. If a perfectly neutral solution of ammonium oxalate is used, the product will have a dull reddish yellow color, from ferric hydrate.

To obtain a bright yellow ferrous oxalate the mother liquor in which the precipitate is formed must be decidedly acid.

Description.—A yellow powder as above, partially insoluble in water, but soluble in acid.

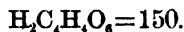
It is permanent in the air at ordinary temperatures, but decomposes, when heated to 155° C., with loss of its water of crystallization.

TARTRATES.

All here described are soluble, but the bitartrates of potassium and sodium are soluble to but a very limited extent. The bitartrates have the property of dissolving ferric hydrate, forming soluble compounds.

TARTARIC ACID.

ACIDUM TARTARICUM.



Tartaric acid occurs in grapes and in other fruits, in the form of acid potassium tartrate, from which it is manufactured.

The following formula, based on Scheele's process, is taken from the British Pharmacopœia:

Potassium bitartrate	900 Gm.
Prepared chalk	250 Gm.
Calcium chloride	270 Gm.
Sulphuric acid	260 C c.
Distilled water, sufficient.	

Boil the potassium bitartrate with 6,500 C.c. of water, and gradually add the chalk, stirring constantly. When effervescence has ceased, add the calcium chloride dissolved in 800 C.c. of water. When the calcium tartrate has subsided, decant the liquid, and wash the tartrate with water until tasteless. Pour the sulphuric acid, previously diluted with 1,200 C.c. of water, on the calcium tartrate, mix thoroughly, boil for half an hour with repeated stirring, and filter through muslin. Evaporate the filtrate at a low temperature until it acquires the specific gravity 1.21, let it cool, and then separate and reject the crystals of calcium sulphate formed. Again evaporate the clear liquid until a pellicle forms, and then set aside to cool and crystallize. Lastly, purify the product by re-crystallization.

Reaction.— $2\text{KHC}_4\text{H}_4\text{O}_6 + \text{CaCO}_3 = \text{CaC}_4\text{H}_4\text{O}_6 + \text{K}_2\text{C}_4\text{H}_4\text{O}_6 + \text{CO}_2 + \text{H}_2\text{O}$; and $\text{K}_2\text{C}_4\text{H}_4\text{O}_6 + \text{CaCl}_2 = \text{CaC}_4\text{H}_4\text{O}_6 + 2\text{KCl}$; finally, $\text{CaC}_4\text{H}_4\text{O}_6 + \text{H}_2\text{SO}_4 = \text{H}_2\text{C}_4\text{H}_4\text{O}_6 + \text{CaSO}_4$.

Notes.—Tartaric acid crystallizes best from a solution containing a small amount of free sulphuric acid. Calcium hydrate can be used instead of calcium carbonate.

Description.—Colorless oblique rhombic prisms, having a sharp but pleasant acid taste. They are readily soluble in water and alcohol, and slightly soluble in ether. The crystals are anhydrous and not deliquescent.

Tests.—The pure crystals must give a perfectly clear solution with water and with three parts of alcohol. The aqueous solution must not be precipitated or colored by hydrogen sulphide or ammonium oxalate.

The solid must burn on platinum when strongly heated, leaving no residue.

Saturating power.—100 parts of tartaric acid neutralize:

Potassium hydrate, 74.66 parts	}	Yielding 150.67 parts of potassium tartrate.
Potassium carbonate, 92 parts		
Potassium bicarbonate, 133.38 parts		
Sodium hydrate, 53.33 parts	}	Yielding 153.38 parts of sodium tartrate.
Sodium carbonate, 190.66 parts		
Sodium bicarbonate, 112 parts		
Ammonia water (10 per cent.), 226.67 parts	}	Yielding 122.67 parts of ammonium tartrate.
Ammonia water, stronger (23 per cent.), 80.95 parts		
Ammonium carbonate, 69.78 parts		

POTASSIUM TARTRATE.

POTASSII TARTRAS.



Potassium bitartrate	380 Gm.
Potassium bicarbonate	200 Gm.

Put the bicarbonate in a dish with about 1,200 C.c. of distilled water; heat until effervescence ceases; keep the solution hot and gradually add the potassium bitartrate until all is dissolved. Neutralize the liquid, or render it very slightly alkaline by potassium carbonate. Filter, evaporate until a pellicle forms, and set aside to crystallize; or evaporate to dryness, with constant stirring.

Reaction.—First the potassium bicarbonate is heated until converted into normal carbonate: $2\text{KHCO}_3 = \text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$; then,
 $2\text{KHC}_4\text{H}_4\text{O}_6 + \text{K}_2\text{CO}_3 = 2\text{K}_2\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O} + \text{CO}_2.$

Notes.—In place of 250 Gm. of bicarbonate, 200 Gm. of carbonate of potassium may be used. The solution must be neutralized by adding more of either the bicarbonate or the bitartrate as may be required. The theoretical proportions are 100 parts of potassium bicarbonate to 183 parts of potassium bitartrate; but it is preferable to use a small excess of bitartrate and to carefully add just enough potassium carbonate at the end to produce a faintly alkaline reaction. The presence of carbonic acid in the liquid should not be allowed to mislead the operator; the litmus paper should be used after the carbonic acid has been driven off by heat. Larger crystals are obtained if the solution is slightly alkaline. The concentration of the solution must not be carried too far, because the salt may then become discolored (by a partial decomposition of the tartaric acid?). The last mother liquor is usually quite colored, and the potassium tartrate contained in it is, therefore, advantageously converted into bitartrate by HCl, the precipitate being washed and dried.

Description.—Monoclinic prisms, soluble in water very readily, but nearly insoluble in cold alcohol. Treated with acetic acid the aqueous solution throws down a white precipitate of bitartrate.

Tests.—The solution in water must be perfectly clear. This, acidified with hydrochloric acid, must not be colored or precipitated by hydrogen sulphide or barium chloride. When the crystals are heated to redness they are completely decomposed, leaving a residue of K_2CO_3 for each molecule of the salt. This residue can be tested by means of standard solution of acid, as described later.

POTASSIUM BITARTRATE.

POTASSII BITARTRAS.



In the manufacture of wine a large amount of impure potassium bitartrate is deposited from the grape juice during the second fermentation, the salt being thrown out of solution by the alcohol formed. Thick crusts are formed in the vats, over the bottom and sides. The bitartrate formed on the bottom contains more calcium salt than that on the sides. The "argols" or "crude tartar" must be powdered, redissolved in boiling water, freed from coloring matter by the addition of clay, which carries it down in settling. The solution is then clarified with albumen, strained, and allowed to deposit crystals. The crystals forming on the sides are again less impure than those on the bottom. Their relative freedom from calcium salt is indicated by their clearness or opacity, the milky opaque crystals being more contaminated with calcium tartrate.

This purified argols or refined tartar is further purified by reducing it to fine powder and digesting this with pure hydrochloric acid diluted with distilled water. The calcium tartrate is then decomposed by the hydrochloric acid, forming calcium chloride and free tartaric acid, both of which are washed out. The mixture is now allowed to cool, so that most of the potassium bitartrate dissolved in the water may deposit again, after which the "cream of tartar" is washed with cold water until the washings cease to give any reaction for chlorides, and then dried. A small percentage of bitartrate is lost by solution in the water with which it is treated.

Description.—Colorless anhydrous crystals, slightly soluble in cold water, but much more readily in warm, insoluble in strong alcohol. From the strong aqueous solution made by heat, crystals separate on cooling as a fine powder. By the process now employed in the United States few substances are made of such remarkable purity as "cream of tartar."

Tests.—The crystals must dissolve completely in 15 to 20 parts of boiling water. 3 Gm. of the salt dissolved by boiling in 100 C.c. of water must require for neutralization 31.6 C.c. of $\frac{N}{4}$ NaOH solution, showing 99 per cent. of the pure acid tartrate.

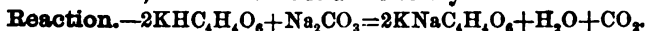
ROCHELLE SALT.

POTASSII ET SODII TARTRAS.



Potassium bitartrate	5 parts.
Sodium carbonate	4 parts.
Distilled water	20 parts.

Heat the water to boiling in a porcelain dish; add the sodium carbonate, and when that is dissolved, gradually add the cream of tartar, and continue heating until all is dissolved. Set the solution aside for a day or two. Then filter, evaporate the filtrate to nine parts, or until a pellicle forms, and then set it aside to crystallize.



Notes.—A slight excess of sodium carbonate is prescribed, because the salt crystallizes best from a slightly alkaline solution. Any excess of sodium carbonate will remain in the mother liquor. Large crystals are easily obtained. The crystals should be hastily rinsed with a little cold distilled water. The mother liquor is usually colored, more so the farther the evaporation is carried. (See also, Potassium Tartrate.)

The direction to allow the solution to stand some time before filtering and evaporating to crystallization, has for its object the deposition of any calcium tartrate present.

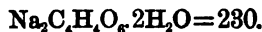
The crystals must be dried without the aid of heat.

Description.—Large clear prisms or fine white powder, very readily soluble in water, but insoluble nearly in alcohol.

Tests.—The crystals must give a clear solution with ten parts of water. This must be neutral in reaction, and not acted upon by ammonium oxalate or ammonium sulphide.

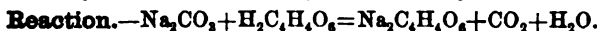
SODIUM TARTRATE.

SODII TARTRAS.



Tartaric acid	10 parts.
Sodium carbonate	19 parts.

Dissolve the acid in 60 parts of distilled water over a water-bath; add the sodium carbonate gradually to the hot liquid, so as to render it neutral or slightly alkaline to test-paper after the carbonic acid has been expelled by heat. Filter, evaporate, and crystallize.



Description.—Clear, colorless, rhombic crystals, permanent in the air, soluble in 5 parts of cold water, insoluble in alcohol, of neutral reaction to test-paper, and having a very mildly saline taste.

SODIUM BITARTRATE.**SODII BITARTRAS.**

Tartaric acid.....	20 parts.
Sodium carbonate.....	19 parts.

Dissolve one-half of the acid in 50 parts of distilled water, neutralize with the sodium carbonate, and filter. Dissolve the other half of the tartaric acid in 50 parts of distilled water and filter. Mix the two liquids. Set the mixture aside in a cool place for a day or two; then collect and dry the precipitated crystalline salt.

MAGNESIUM TARTRATE.**MAGNESII TARTRAS.**

Tartaric acid.....	10 parts.
Magnesium carbonate	6 parts.

Dissolve the acid in 20 parts of distilled water, keep the solution hot over a water-bath, and add gradually the magnesium carbonate until a neutral salt is obtained. Evaporate to dryness, and powder the residue.

Description.—A white powder, which is difficultly water soluble.

TARTRATE OF IRON AND POTASSIUM.**FERRI ET POTASSII TARTRAS.**

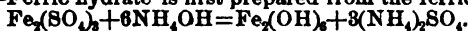
Solution of normal ferric sulphate	12 parts.
Potassium bitartrate.....	4 parts.
Distilled water	32 parts.
Ammonia water, sufficient.	

Mix 10 parts of ammonia water with 20 parts of cold water; add gradually, and with constant stirring, the solution of tersulphate of iron, previously diluted with 100 parts of cold water. Pour the mixture on a wet muslin strainer, allow the magma to drain, and then return it to the precipitating vessel and mix it well with 100 parts of cold water. Drain it again on the strainer, and repeat this operation once or twice,

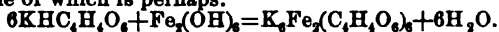
as may be necessary, until the washings produce but a slight cloudiness with test solution of barium chloride. Let the magma be well drained. Add it in small portions at a time to a mixture of the distilled water and the potassium bitartrate, heated over a water-bath at not over 60° C. (140° F.), stirring constantly until all the ferric hydrate has been added and dissolved. Filter while hot and set the filtrate aside in a cool, dark place for twenty-four hours; then stir it well with a porcelain or glass stirrer until any precipitate which may have formed in the liquid is evenly distributed through it. Then cautiously add just enough ammonia water to dissolve this precipitate, filter, and evaporate the solution in a porcelain dish to the consistence of thick syrup, and spread it on glass plates to dry in scales.

Keep the product in well corked amber bottles, in a dark place.

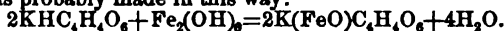
Reaction.—Ferric hydrate is first prepared from the ferric sulphate:



Ferric hydrate is then dissolved by the potassium tartrate, forming several double salts, one of which is perhaps:



while another is probably made in this way:



Notes.—Whether prepared from solution of tersulphate of iron or from solution of chloride of iron, the ferric hydrate must be carefully precipitated, from cold dilute solutions, and well washed. When made from chloride it is more readily washed clean. The hydrate does not dissolve rapidly in the liquid, or the soluble tartrate of iron and potassium is but slowly formed from the ferric hydrate and the potassium bitartrate. Several hours are required to complete the solution. In view of the fact that ferric hydrate is so liable to become basic and insoluble when subjected to heat, it is best to add the ferric hydrate in portions, to regulate the heat carefully, and to stir constantly. The success of the whole process depends to a great extent upon the character of the ferric hydrate and upon the precautions described in the foregoing. The addition of ammonia is intended to render the product readily water soluble without residue. The Pharmacopœia does not direct that the solution should be filtered, but this is necessary to obtain a good product.

Description.—Transparent red scales, soluble in water, but not in alcohol. The solution in water is not precipitated by ammonium hydrate. It is precipitated when heated with solutions of potassium or sodium hydrate.

The salt is decomposed by heat, leaving a strongly alkaline residue, which effervesces with acids.

TARTRATE OF IRON AND AMMONIUM.

FERRI ET AMMONII TARTRAS.



Solution of normal ferric sulphate	90 parts.
Tartaric acid	60 parts.
Ammonia water	72 parts.
Ammonium carbonate, distilled water, each sufficient.	

Mix the ammonia water with 180 parts of cold water; add gradually, and with constant stirring, the solution of tersulphate of iron previously diluted with 900 parts of cold water.

Pour the mixture on a wetted muslin strainer, allow the magma to drain, and then return it to the precipitating vessel and mix it well with 1,000 parts of cold water. Drain it again on the strainer, and repeat the operation once, or oftener, until the washings only give a slight cloudiness with barium chloride solution. Then allow it to drain thoroughly. Dissolve one-half of the tartaric acid in 130 parts of distilled water, neutralize the acid exactly with ammonium carbonate, then add the remainder of the tartaric acid, and dissolve it by the aid of heat. Keep the solution of ammonium bitartrate hot, but not above 60°C (140°F .), over a water-bath, and add to it, with constant stirring, the ferric hydrate, in small portions at a time, until no more will dissolve. Filter the solution, evaporate it at not over 60°C . to the consistence of syrup, and spread it on glass plates to dry in scales.

Keep the product in amber-colored bottles, tightly corked, and put in a cool, dark place.

Notes.—The remarks under Tartrate of Iron and Potassium apply in a general way to this process as well. The ammonium bitartrate is $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$, by which the ferric hydrate is dissolved in a manner analogous to the solution effected by digesting the hydrate with potassium bitartrate in making the tartrate of iron and potassium.

Description.—Transparent scales like the preceding, but sometimes lighter in color.

The general properties are the same.

When heated with solution of potassium hydrate, ammonia is given off and ferric hydrate is precipitated. The dry salt, when strongly heated, leaves a residue which does not effervesce with acids, and which is without alkaline reaction.

TARTRATE OF ANTIMONY AND POTASSIUM.

ANTIMONII ET POTASSII TARTRAS.



Oxide of antimony	4 parts.
Potassium bitartrate	5 parts.
Water	50 parts.

Mix the oxide and the cream of tartar with enough water to form a paste, and set this aside for twenty-four hours. Then add the remainder of the water and boil the mixture in a porcelain capsule for fifteen minutes, stirring frequently, and replacing the water lost by evaporation. Filter while hot, evaporate the filtrate to 30 parts, and set it aside to crystallize. Wash the crystals with a little cold water, and then dry them between filter paper.

Reaction.— $2\text{KHC}_4\text{H}_4\text{O}_6 + \text{Sb}_2\text{O}_3 = 2\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 + \text{H}_2\text{O}$.

Notes.—A slight excess of antimonious oxide is used, but remains undissolved and is filtered away. To obtain the salt in minute crystals the solution obtained by the above formula may be evaporated down to 27 parts and then shaken in a bottle until cold, when the greater part of the salt will separate. The mother liquor will yield more crystals, but after two or three crystallizations it becomes quite colored, as is the case in making several other tartrates.

Description.—Small transparent crystals or white powder, soluble in cold, much more readily in boiling water, but insoluble in alcohol. The solution in hydrochloric acid is precipitated orange red by hydrogen sulphide. In contact with nascent hydrogen the salt should not liberate even traces of hydrogen arsenide, the reactions for which are given later.

BORO-TARTRATE OF POTASSIUM.

POTASSII BORO-TARTRAS.

Potassium bitartrate.....	4 parts.
Boric acid	1 part.
Boiling water.....	10 parts.

Heat together with constant stirring until dissolved. Filter, and evaporate to dryness.

Powder the residue.

Description.—A white powder having an agreeable acidulous taste. It is not deliquescent. Soluble in twice its weight of water; insoluble in alcohol.

BORAX TARTAR.

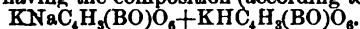
TARTARUS BORAXATUS.

[BORO-TARTRATE OF POTASSIUM AND SODIUM.]

Borax, in powder.....	2 parts.
Potassium bitartrate	5 parts.
Boiling water.....	20 parts.

Put the salts in the water, contained in a porcelain dish, and stir until all is dissolved. Filter. Evaporate the solution until a thread of the semi-liquid residue becomes brittle on cooling. Then pull it into sticks, or flatten it out in thin cakes, and dry it by the aid of heat. Powder the product in a warm mortar, and keep it in tightly closed bottles.

Notes.—In some Pharmacopœias the proportions are 1 part of borax to 2 parts of cream of tartar. There is undoubtedly a chemical union of some kind between the two salts, but the product is not a definite chemical compound. However, when 1 part of borax and 8 parts of potassium bitartrate are combined, a double salt is formed having the composition (according to Duve)



It is sometimes directed that the cream of tartar should be added gradually to the borax previously dissolved in the water. This is not only unnecessary, but delays the operation considerably. If both salts are added at once the solution of both is far more rapid than the solution of borax alone would be. Constant stirring is, however, necessary, because otherwise the borax on the bottom of the dish cakes together and afterwards dissolves rather slowly.

Water-bath heat is insufficient for evaporating the solution to dryness; steam-heat and constant stirring must be employed. Having evaporated the solution to dryness we have a yellowish gummy residue, which on cooling has a glassy fracture. This is then dried in thin cakes or threads at 70° C. (158° F.); it is sufficiently dry when white and porous.

To powder the product fine is both difficult and disadvantageous; it should only be reduced to a very coarse powder, in a warm mortar, and then at once put into warm, dry bottles which must be tightly corked.

Description.—A coarse, white powder, dry, very deliquescent, soluble in its own weight of cold water, but insoluble in alcohol. It has a pleasant acidulous taste.

CHAPTER XXV.

CITRATES.

The citrates are generally soluble salts. Many iron compounds which are not water soluble dissolve in aqueous solutions of alkali citrates. Bismuth citrate is insoluble in water, but soluble in ammonia water.

CITRIC ACID.

ACIDUM CITRICUM.



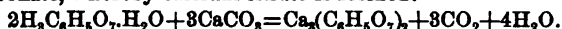
Contained in various plant juices, especially of lemons, limes, and currants. The juice is allowed to ferment enough to decompose the sugar. Then follows clarification with albumen, after which the juice is treated with prepared chalk, and the calcium citrate decomposed with sulphuric acid.

The British Pharmacopœia gives the following working formula:

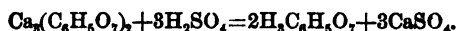
Lemon juice	800 C.c.
Prepared chalk	45 Gm.
Sulphuric acid	25 C.c.

Heat the lemon juice to the boiling point, and gradually add the chalk until it no longer causes effervescence. Collect the deposit on a muslin strainer and wash it with hot water till the filtered liquid passes colorless. Mix the deposited calcium citrate with 200 C.c. of water, and gradually add the sulphuric acid previously diluted with 300 C.c. of water. Boil gently for half an hour, keeping the mixture constantly stirred. Separate the acid solution by filtration, wash the insoluble matter with a little distilled water, and add the washings to the solution. Concentrate this solution to the density of 1.21, then allow it to cool, and after twenty-four hours decant the liquor from the crystals of calcium sulphate which have formed, continue the evaporation of the solution until a pellicle forms, and then set aside to cool and crystallize. If necessary, purify the acid by recrystallization.

Reaction.—The free citric acid in the lemon juice is neutralized by the calcium carbonate, whereby calcium citrate is formed:



When the calcium citrate is treated with sulphuric acid, the following reaction occurs:



Notes.—A small amount of acid calcium citrate always remains in the liquid after the treatment with chalk. This acid salt prevents the precipitation of coloring matter, and after the removal of the neutral calcium citrate, the acid citrate can be decomposed by milk of lime, yielding neutral citrate.

The precipitated calcium citrate is washed with warm water until the washings are nearly colorless. After cooling, it is decomposed by sulphuric acid added in excess to prevent the formation of acid citrate, which would prevent crystallization of the citric acid. The calcium sulphate is washed and then thrown away; but the last of the calcium sulphate does not separate until the solution has been evaporated down to 1.21 sp. gr. The final evaporation to crystallization must not be carried too far, as the free sulphuric acid present would then blacken the product when sufficiently concentrated to decompose the citric acid.

Recrystallization is necessary to render the crystals colorless and pure. Sometimes the solution must be decolorized by animal charcoal.

Description.—Clear rhombic prisms, which are permanent in dry air, but which lose water by elevation of temperature, and at a high heat, above 150° C., decompose, giving off empyreumatic vapors. The crystals have a pleasant acid taste, and are readily soluble in water and alcohol.

Tests.—The solution in water should be perfectly clear.

An acid not perfectly soluble should be dissolved with addition of hydrochloric acid. This solution can be used for detection of lead or copper by addition of hydrogen sulphide, or of iron by means of potassium ferrocyanide. Calcium is best detected as oxalate in the solution first made neutral by ammonia water, and then acid by acetic acid, on addition of ammonium oxalate.

Sulphuric acid is detected in the solution by addition of barium chloride.

The pure acid should leave no ash on incineration.

For neutralization 1.75 Gm. requires 50 C.c. of half normal sodium hydrate solution.

Saturating power.—100 parts of citric acid will saturate :

Potassium carbonate (81 per cent.), 121.69 parts	}	Yielding 154.29 parts of tri-potassium citrate.
Potassium bicarbonate, 142.86 parts		
Sodium carbonate (96 per cent.), 212.80 parts	}	Yielding 178.57 parts of tri-sodium citrate.
Sodium bicarbonate (99 per cent.), 121.21 parts		
Ammonia water (10 per cent.), 242.86 parts	}	Yielding 124.29 parts of tri-ammonium citrate.
Ammonia water, stronger (28 per cent.), 86.78 parts		
Ammonium carbonate, 74.76 parts		

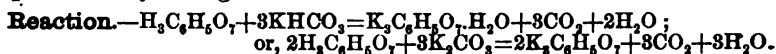
POTASSIUM CITRATE.

POTASSII CITRAS.



Potassium bicarbonate	10 parts.
Citric acid	7 parts.

Crush the citric acid and the bicarbonate, separately; add the latter gradually to 50 parts of boiling water, and when effervescence ceases add the citric acid, a small portion at a time, until the liquid is neutral to litmus paper, or but faintly alkaline. Filter, and evaporate to dryness, stirring constantly after a pellicle has commenced to form, so that the product may be a granular salt.



Notes.—The temperature must not be too high toward the close of the evaporation, as citric acid and citrates are decomposed at a high heat.

Description.—Small glassy needles or fine granular powder, with slightly alkaline taste. The salt is deliquescent, and insoluble in absolute alcohol.

The solution boiled with a solution of calcium chloride gives a precipitate of calcium citrate.

Tests.—The reaction of the aqueous solutions should be slightly alkaline; treated with dilute acids there should be no effervescence.

The solution acidified with nitric acid should not be precipitated by barium chloride or silver nitrate.

SOLUTION OF POTASSIUM CITRATE.

LIQUOR POTASSII CITRATIS.

Citric acid	6 parts.
Potassium bicarbonate	8 parts.

Dissolve each in 40 parts of cold water. Filter the solutions separately, and wash the filters with enough water to obtain, in each case, 50 parts of filtrate. Mix the two solutions, and, when effervescence has ceased, put the product in a bottle and cork it tightly.

Should be freshly prepared whenever required for use.

Notes.—It is intended that cold water should be used, and that the preparation should retain in solution as much of the carbonic acid as may be soluble in that volume of the watery liquid. An excess of citric acid is purposely employed in order that the preparation may have a slightly acidulous taste.

SOLUTION OF NORMAL SODIUM CITRATE.

LIQUOR SODII CITRATIS.

Each C.c. contains about 0.50 Gm. of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$.

Citric acid	400 Gm.
Sodium bicarbonate	486 Gm.

Dissolve the sodium bicarbonate in 750 C.c. of distilled water by the aid of heat, gradually add the citric acid, and, when effervescence has ceased, bring the liquid to the boiling point. If the solution is not neutral to litmus paper, add more sodium bicarbonate (or citric acid, as the case may require) to produce a perfectly neutral reaction. Finally, add enough distilled water to make the whole measure 1,080 C.c.

To make solution of *di-sodium-hydrogen citrate*, containing 0.50 Gm. of $\text{Na}_2\text{HC}_6\text{H}_5\text{O}_7$, in each C.c. add 200 Gm. of citric acid to 1,080 C.c. of the above solution, and finally add enough distilled water to make the whole product measure 1,480 C.c.

Used in making certain scale salts of iron.

LITHIUM CITRATE.

LITHII CITRAS.

$\text{Li}_3\text{C}_6\text{H}_5\text{O}_7 = 210$.

Lithium carbonate	10 Gm.
Citric acid	19 Gm.
Water	200 C.c.

Dissolve, filter, and evaporate to granulation.

Reaction.— $3\text{Li}_2\text{CO}_3 + 2\text{H}_3\text{C}_6\text{H}_5\text{O}_7 = 2\text{Li}_3\text{C}_6\text{H}_5\text{O}_7 + 3\text{H}_2\text{O} + 3\text{CO}_2$.

SOLUTION OF NORMAL AMMONIUM CITRATE.

LIQUOR AMMONII CITRATIS.

Each C.c. contains about 0.50 Gm. of $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$.

Citric acid	500 Gm.
Stronger water of ammonia	430 C.c.

Dissolve the acid in the ammonia water. Neutralize perfectly by adding as much ammonia water as may be necessary. Then add enough distilled water to make the whole measure 1,250 C.c.

To make solution of *di-ammonium-hydrogen citrate* add 250 Gm. of citric acid to 1,250 C.c. of the above solution and enough distilled water to make the whole measure 1,800 C.c.

Used in preparing certain scale salts of iron. Solution of citrate of ammonium also has the remarkable property of dissolving or preventing precipitates in many preparations containing iron salts, as in wine of beef and iron, elixir of phosphate of iron, quinine and strychnine, etc.

MAGNESIUM CITRATE.

MAGNESII CITRAS.

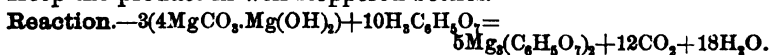


In the Swedish Pharmacopœia occurs a magnesium citrate of the formula indicated, but mixed with an excess of citric acid amounting to about 9 per cent. It is prepared as follows:

Magnesium carbonate, in powder.....	5 parts.
Citric acid, in fine powder.....	8 parts.
Alcohol.....	12 parts.

Mix the magnesium carbonate and acid intimately by trituration in a mortar, and add the alcohol, mixing the whole well so as to form a pasty mass free from lumps. Cover the mortar loosely with paper, and set it aside until the alcohol has evaporated, leaving a dry residue, which must be at once reduced to powder.

Keep the product in well stoppered bottles.



Notes.—To insure as complete a chemical union as practicable the citric acid might be dissolved in the alcohol, and the magnesium carbonate added in small quantities at a time. On the addition of the magnesium carbonate the temperature of the mixture falls considerably. The mixture soon becomes a hard mass unless triturated without interruption until rendered perfectly homogeneous. The carbonic acid escapes with effervescence, and the alcohol is added to facilitate the reaction and the liberation of the gas. To prevent too rapid dissipation of the alcohol, the mass is allowed to dry by spontaneous evaporation, and it is better to spread the moist mass in an even layer upon paper than to dry it in a heap in the mortar, because it is essential that the drying be uniform, otherwise some portions of the preparation become very hard and dissolve with difficulty in water. A small amount of water must remain in the product in order to render it readily water soluble. It should, therefore, be dried only sufficiently to make its pulverization possible, and to prevent its caking together after being bottled.

Description.—A white powder, entirely but rather slowly soluble in 10 parts of water, requiring about 10 minutes to dissolve. The solution is not permanent, however, basic salts soon separating. This decomposition is prevented by the presence of alkali citrates. An unclear solution may be rendered clear by gently heating it, and does not become turbid again for several days.

GRANULATED MAGNESIUM CITRATE.**MAGNESII CITRAS GRANULATUS.**

Magnesium carbonate.....	11 parts.
Citric acid.....	48 parts.
Sodium bicarbonate.....	37 parts.
Sugar, in No. 60 powder.....	8 parts.
Alcohol, distilled water, each sufficient.	

Mix the magnesium carbonate and 33 parts of citric acid with enough distilled water to make a thick paste; dry this at not over 30° C (86° F.) and reduce it to a fine powder. Then mix it intimately with the sugar, the sodium bicarbonate, and the remainder of the acid previously reduced to a very fine powder. Dampen the mass with a sufficient quantity of alcohol, and rub the damp mixture through a No. 20 sieve of tinned iron, to form a coarse granular powder. Lastly, dry it in a moderately warm place.

Keep the product in well closed bottles.

Notes.—By reference to the preceding notes under the title Magnesium Citrate it will be seen that the first part of the process has for its object the formation of normal magnesium citrate. This is then dried, powdered, and mixed with powdered sugar, sodium bicarbonate and citric acid. The citric acid must be finely powdered. It is necessary that these ingredients should be very thoroughly mixed before the alcohol is added, and only enough alcohol to dampen the mixture should be used. The small amount of water contained in the normal magnesium citrate and in the alcohol is sufficient to cement the particles of powder together into little granules, and the coarse powder is run through a No. 20 sieve to make it more uniform. As a brass sieve would be attacked by the compound, a tinned iron sieve is directed to be employed. The sodium bicarbonate is not decomposed by the citric acid, in the dry mixture, and hence the preparation, when dissolved in water, yields an effervescing drink.

Description.—A white, coarsely granular mixture, deliquescent on exposure to air, inodorous, having a mildly acidulous taste and acid reaction. Soluble, with copious effervescence, in two parts of water; nearly insoluble in alcohol. The aqueous solution contains sodium-magnesium citrate, some free carbonic acid, citric acid, and sugar.

VARIETIES OF MAGNESIUM CITRATE.

Hager states that normal magnesium citrate occurs in three forms, differing from each other in the proportion of water they contain, and in solubility. *Amorphous* magnesium citrate contains 2 to 3 molecules of water, and is soluble in 2 parts of water at ordinary temperatures; *metamorphous* magnesium citrate contains about 5 molecules of water, and is soluble in 10 parts of water; and the *crystalline* magnesium citrate contains 7 molecules of water, and requires 100 parts of water for its solution. The amorphous variety, when in watery solution, gradually changes to the crystalline form, passing through the metamorphous form, this alteration being usually completed in from three to five days.

The changes referred to are, at least, partially prevented by the presence of alkali-citrates.

SOLUTION OF MAGNESIUM CITRATE.

LIQUOR MAGNESII CITRATIS.

Contains $\text{MgHC}_6\text{H}_5\text{O}_7$.

Magnesium carbonate	13 Gm.
Citric acid	26 Gm.
Syrup of citric acid	65 C.c.
Potassium bicarbonate	2 Gm.

Dissolve the citric acid in 120 C.c. of water, add the magnesium carbonate, and stir until dissolved. Filter the solution into a strong bottle of the capacity of 360 C.c., and containing the syrup. Then add enough water, previously boiled and filtered, to nearly fill the bottle, drop into it the potassium bicarbonate, and immediately insert the cork, securing it with twine. Lastly, shake the mixture occasionally until the potassium bicarbonate is dissolved.



Notes.—Acid magnesium citrate, which is contained in this preparation, does not yield any deposit of magnesium salt such as is formed after about three days in solutions of normal magnesium citrate. As calcium citrate is insoluble in water, the magnesium carbonate and the water used ought perhaps to be free from lime. Acid calcium citrate is, however, soluble to a limited extent. It is directed in the Pharmacopoeial working formula that the water added last shall be “previously boiled and filtered.” As this precaution has for its object the removal of any lime present, the same treatment should be applied to the whole of the water used, if it be intended that the preparation shall be free from calcium salt, for all of the calcium citrate formed from the calcium carbonate present in the water will dissolve in the excess of citric acid used, unless the water employed is quite “hard,” in which case it is unfit for use. Heat materially hastens the solution of the acid and the magnesium carbonate, and with the quantity of citric acid taken no harm will result if the water in which the acid is dissolved be hot, and the heat continued until the magnesium carbonate has dissolved. The solution should then be filtered, and allowed to become quite *cold* before the other ingredients are added. The clear syrup should be first put in the bottle; then the filtered acid solution of magnesium citrate carefully added so as not to mix it with the layer of syrup covering the bottom of the bottle; then the bottle should be *nearly* filled with water, and the potassium bicarbonate, in large clear crystals, dropped in, after which the cork is at once driven into the neck of the bottle.

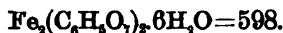
The bottles used for this preparation are made strong enough to bear the pressure caused by the carbonic acid liberated from the potassium bicarbonate by the citric acid. They must necessarily be of such size as to be nearly filled by the solution when finished and of proper strength. The corks used must be about $1\frac{1}{2}$ inches long, and of the finest quality, as large as they can possibly be used, and soaked in hot water so as to be soft and elastic when inserted; the soaked corks ought to be fitted to the necks of the bottles when the latter have been cleaned, but while still empty, and should be so large that, after using the cork presser, they can be driven in by one or two smart blows with a mallet, closing the bottles perfectly. The wire or twine used to tie the corks down securely must be properly attached to the necks of the bottles beforehand, leaving a loop on one side long enough to reach to the center of the top of the cork, and the two ends on the opposite side, so that as soon as the cork has been driven in rather more than one-half its length, it can be at once tied over.

The quantity of potassium bicarbonate used can be advantageously increased to 2.50 Gm., so that the solution may be well charged with carbonic acid: The bottles should be laid on their sides in a cool place, taking care not to shake the contents so as to mix the syrup with the lighter watery solution. The potassium bicarbonate will then rest in the syrup, and dissolve but slowly. When required for use, the bottle is shaken until all of the bicarbonate is dissolved. Solution of citrate of magnesium is rather agreeable to the taste when properly made, fresh, and cold. It loses its agreeable taste entirely when kept in a warm place, when kept too long, or when taken without first being properly cooled on ice or otherwise.

Magnesium oxide may be employed instead of magnesium carbonate, using only one-half as much of the oxide. But the carbonate is less variable in composition.

FERRIC CITRATE.

FERRI CITRAS.



Evaporate any convenient quantity of the solution of ferric citrate over a water-bath at a temperature not exceeding 60° C. (140° F.) to the consistence of thick syrup, and spread it on glass plates to dry in scales.

Keep it in well stoppered bottles in a cool, dark place.

Description.—Thin, garnet red scales, soluble in hot water, slowly in cold, and insoluble in alcohol.

The reaction of the solution is acid.

Tests.—Must not be precipitated by ammonia water.

When incinerated an ash is left, which when treated with water should not give an alkaline reaction.

SOLUTION OF FERRIC CITRATE.

LIQUOR FERRI CITRATIS.

Contains about 35.5 per cent. of $\text{Fe}_2(\text{C}_6\text{H}_5\text{O}_7)_3$, 490.

Solution of normal ferric sulphate.....	21 parts.
Citric acid.....	6 parts.
Ammonia water.....	18 parts.

Mix the ammonia water with 40 parts of cold water, and the iron solution with 200 parts of cold water. Add the cold dilute iron solution gradually to the ammoniacal liquid, stirring constantly. Let the precipitated ferric hydrate settle somewhat, and decant the supernatant liquid. Pour the remainder of the mixture, containing the precipitate, upon a wetted muslin strainer, let it drain, and then return the precipitate to the precipitating vessel, and mix it well with 240 parts of cold water. Let settle, decant, and again drain the magma on the muslin strainer.

Repeat this washing process until the washings give but a slight cloudiness when mixed with test solution of barium chloride. Then let the mass be thoroughly drained. Transfer the moist ferric hydrate to a porcelain dish, add the citric acid, and heat the mixture over a water-bath to 60° C. (140° F.), stirring constantly, until the ferric hydrate is dissolved. Lastly, filter the solution, and evaporate it at not over 60° C. until it weighs 20 parts.

Reaction.—First: $\text{Fe}_2(\text{SO}_4)_3 + 6\text{NH}_4\text{OH} = \text{Fe}_2(\text{OH})_6 + 3(\text{NH}_4)_2\text{SO}_4$; then, $\text{Fe}_2(\text{OH})_6 + 2\text{H}_2\text{C}_6\text{H}_5\text{O}_7 = \text{Fe}_2(\text{C}_6\text{H}_5\text{O}_7)_2 + 6\text{H}_2\text{O}$.

Notes.—The necessity of using cold dilute solutions for making the ferric hydrate has been pointed out under the title, Ferric Hydrate.

In some respects the official formula given above may be advantageously modified. Thus the water retained by the magma after washing ought to be pressed out by means of a strong press, until the weight of the pressed hydrate is equal to three-fourths of the prescribed weight of the final product. The citric acid should at the same time be dissolved in 20 parts of water, and this solution kept at a temperature not exceeding 60° C. (140° F.) in a porcelain dish over a water-bath. The ferric hydrate should be added in portions, a little at a time, the liquid being constantly stirred, and each portion of ferric hydrate added should be allowed to dissolve before adding more. The application of heat is necessary because the citric acid will not become saturated with ferric hydrate at ordinary temperatures, dissolving it very slowly, and because a solution of normal ferric citrate dissolves ferric hydrate, forming basic salts at common but not at higher degrees of heat. Ferric hydrate, however, is sensitive to heat, and partly rendered basic and insoluble if exposed a considerable time to the heat required for saturating the citric acid in this process. For these reasons the ferric hydrate should be added in small quantities at a time so as not to be long exposed to heat before it is dissolved. The presence of even traces of ammonia will considerably facilitate the solution of the ferric hydrate. In order to obtain satisfactory results the citric acid should be saturated, and hence ferric hydrate used in excess. The hydrate finally remaining undissolved is altered by the heat, acquiring a yellowish color, and is readily filtered away.

Some good pharmacists prefer to use ferric chloride instead of ferric sulphate in preparing the ferric hydrate for this preparation, and for all scale salts of iron.

The presence of any considerable excess of citric acid in this preparation is objectionable, because it will then be unfit for use in preparing scaled preparations, the acid solution adhering to the glass plates like a tough varnish, or drying in powder instead of scales.

Description.—A dark brown solution, having a specific gravity of 1.26; sp. vol. 0.793. One hundred parts of this solution yield about forty-four parts of scales as previously described.

Tests.—Gives a red brown precipitate when boiled with alkalis. With potassium ferrocyanide it gives a greenish color, becoming deep blue on addition of hydrochloric acid.

When boiled with sodium or potassium hydrate, ammoniacal vapors should not be given off.

AMMONIO-FERRIC CITRATE.

FERRI ET AMMONII CITRAS.

Composition not determined.

Solution of ferric citrate	3 parts.
Ammonia water	1 part.

Mix and evaporate the mixture over a water-bath at not over 60° C. (140° F.) to the consistence of thick syrup; spread this on glass plates and let it dry in scales.

Keep the product in a well stoppered bottle, in a cool, dark place.

Notes.—For making this preparation some formulas prescribe that three parts of citric acid dissolved in water be saturated with ferric hydrate as described in the notes under Solution of Ferric Citrate, and that one part of citric acid, saturated with ammonia, be afterwards added, and the solution evaporated to form scales. The working formula of the Norwegian Pharmacopœia is so framed.

Description.—In its general appearance and behavior it is similar to the simple iron salt.

Tests.—Yields ammonia when boiled with strong solution of sodium hydrate. The ash should not show an alkaline reaction when heated with water.

CITRATE OF IRON AND QUININE; U. S.

FERRI ET QUININÆ CITRAS; U. S.

Ferric citrate	22 parts.
Quinine, dried at 100° C. (212° F.), until it ceases to lose weight.	3 parts.

Dissolve the ferric citrate in 30 parts of distilled water in a porcelain dish over a water-bath at not over 60° C. (140° F.). Add the alkaloid and stir constantly until dissolved. Evaporate at the temperature named until the liquid is reduced to the consistence of syrup, and spread it on glass plates to dry in scales. Keep the product in well stoppered bottles, in a cool, dark place.

Notes.—This, the official citrate of iron and quinine of the United States, is reddish brown and only slowly, though perfectly, water soluble. The most commonly employed citrate of iron and quinine, however, is that prepared with the addition of ammonia, by which the preparation is not only rendered more readily soluble but changed also in color, being greenish yellow.

The quinine should be finely divided, and ought to be triturated with a portion of cold solution of the citrate of iron, being afterwards well mixed with the whole before the digestion begins. Otherwise it may run together in lumps, which, afterwards, are very difficult to dissolve.

In this, as in all other scale salts of iron, it is necessary that no considerable excess of free citric acid should be contained in the preparation, for then the salt will not form scales, but adheres like a varnish to the glass plates. For this reason the official formula, prescribing the use of already scaled ferric citrate, is less liable to result in failure than a formula in which solution of citrate of iron is used.

"Quinine dried at 100° C. (212° F.), until it ceases to lose weight," is monohydrated quinine ($C_{20}H_{24}N_2O_2 \cdot H_2O$). The drying at this temperature is directed for the purpose of insuring uniformity.

Description.—Transparent scales, reddish to yellowish brown, slowly deliquescent on exposure to air, odorless, having a bitter and mildly ferruginous taste, and slightly acid reaction. Slowly but wholly soluble in cold water, more readily so in hot water, and but slightly soluble in alcohol. When strongly heated, the salt emits fumes having the odor of burnt sugar, and finally leaves a residue which should not have an alkaline reaction (absence of fixed alkalies).

Tests.—On supersaturating the aqueous solution of the salt with a slight excess of ammonia, the color of the liquid is deepened and a white, curdy precipitate is thrown down, which is soluble in ether and answers to the reactions of quinine given later.

A small portion of the filtrate, when mixed with solution of ferrocyanide of potassium, does not produce a blue color or precipitate unless it is acidulated with hydrochloric acid.

CITRATE OF IRON AND QUININE; B.

FERRI ET QUININÆ CITRAS; B.

Solution of normal ferric sulphate.....	250 C.c.
Sulphate of quinine.....	40 Gm.
Diluted sulphuric acid.....	60 C.c.
Citric acid.....	124 Gm.
Ammonia water, distilled water, each sufficient.	

Mix 320 C.c. of ammonia water with 1,600 C.c. of cold water; add to this the solution of ferric sulphate, also previously diluted with 1,600 C.c. of cold water, stirring constantly and briskly. Let the mixture stand for two hours, stirring it occasionally; then transfer it to a wetted muslin strainer, and, when thoroughly drained, wash the hydrate with water until the washings cease to give a precipitate with barium chloride.

Mix the quinine sulphate with 320 C.c. of water, add the diluted sulphuric acid, and, when the salt is dissolved, precipitate the quinine with a slight excess of ammonia water. Collect the precipitate on a filter, and wash it with 1,000 C.c. of distilled water.

Dissolve the citric acid in 200 C.c. of distilled water, heated on a water-bath; add the ferric hydrate, previously well drained; stir them together, and, when the hydrate has dissolved, add the precipitated quinine, continuing the stirring until the alkaloid has also dissolved. Let the mixture cool. Add cautiously, a little at a time, 60 C.c. of ammonia water previously diluted with 80 C.c. of distilled water, stirring briskly, and allowing the quinine which separates with each addition of ammonia to re-dissolve before adding another portion. Filter the solution, evaporate it to the consistence of a thin syrup, and spread it on glass plates to dry in scales at not over 40° C. (104° F.).

Notes.—The product is in greenish golden yellow scales, somewhat deliquescent, and readily soluble in water. It contains 16 per cent. of the alkaloid quinine.

CITRATE OF IRON AND QUININE; G. P.

CHININUM FERRO-CITRICUM; G.

Citric acid.....	6 parts.
Powdered iron.....	3 parts.
Quinine.....	1 part.

Dissolve the citric acid in 500 parts of water, heated in a porcelain dish; add the iron and digest over a water-bath, with frequent stirring, for 48 hours. Filter. Evaporate the filtrate to 50 parts, and then add the quinine. When the alkaloid has dissolved, evaporate to a syrupy consistence and spread it on glass plates to dry in scales.

Notes.—This preparation contains both ferrous and ferric citrate. The quinine should be recently precipitated from a solution of 1.3 parts of quinine sulphate, dissolved in water with the aid of dilute sulphuric acid, the precipitant being sodium hydrate.

CITRATE OF IRON AND QUININE; SW.

CITRAS FERRICO-CHINIOSUS; PH. SU.

The working formula of the Swedish Pharmacopœia is as follows:

Citric acid	13 parts.
Ferric chloride	12 parts.
Quinine	3 parts.
Ammonia water	57 parts.

Dissolve the ferric chloride in 400 parts of cold water, and pour the solution into a mixture of the ammonia water and 60 parts of water. Wash the ferric hydrate thoroughly, and press out the moisture from it. Dissolve the citric acid in 25 parts of distilled water, warm the solution over a water-bath at not above 40° C. (104° F.), and add, during constant stirring, the ferric hydrate in small portions at a time until the citric acid is saturated. Then add the quinine in the manner prescribed in the notes under Citrate of Iron and Quinine, U. S.

SOLUTION OF CITRATE OF IRON AND QUININE.

LIQUOR FERRI ET QUININÆ CITRATIS.

Ammonio-ferric citrate	65 parts.
Quinine, dried at 100° C. (212° F.) until it ceases to lose weight	12 parts.
Citric acid	28 parts.
Alcohol	30 parts.

Dissolve the citrate of iron and ammonium in 200 parts of distilled water, in a tared porcelain dish; heat the solution over a water-bath to 60° C. (140° F.), add the citric acid, and, when this has dissolved, add the alkaloid previously triturated to a homogeneous mixture with a cooled portion of the liquid, and continue stirring until a perfect solution results. Evaporate to 160 parts, let cool, add the alcohol, and finally 10 parts of distilled water.

Should be kept in a well stoppered bottle, in a cool, dark place.

CITRATE OF IRON AND STRYCHNINE.**FERRI ET STRYCHNINÆ CITRAS.**

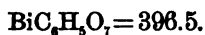
Citrate of iron and ammonium	98 parts.
Strychnine	1 part.
Citric acid	1 part.

Dissolve the ammonio-ferric citrate in 100 parts of distilled water; and the alkaloid, together with the citric acid, in 20 parts of distilled water. Mix. Evaporate the mixture by water-bath at not over 60° C. (140° F.) to a syrupy liquid, and spread this on glass plates to dry in scales.

Keep the product in well stoppered bottles, in a cool, dark place.

Description.—Transparent, garnet-red scales, deliquescent on exposure to air, odorless, having a bitter and slightly ferruginous taste, and a slightly acid reaction. Readily and wholly soluble in water, and but slightly soluble in alcohol. When strongly heated, the salt emits fumes having the odor of burnt sugar, and finally leaves a residue which should not have an alkaline reaction (fixed alkalies). On heating the aqueous solution of the salt with solution of potassa, a brown red precipitate is produced and vapor of ammonia is evolved.

Tests.—If 1 Gm. of the salt be dissolved in 4 C.c. of water, in a small test-tube, then 1 C.c. of solution of potassa added, and the mixture shaken with 2 C.c. of chloroform, the residue left on evaporating the chloroform will answer to the reactions of strychnine given later. The solution made acid by hydrochloric acid is colored blue by potassium ferrocyanide.

BISMUTH CITRATE.**BISMUTHI CITRAS.**

Bismuth subnitrate	10 parts.
Citric acid	7 parts.

Boil them with 40 parts of distilled water until a drop of the mixture yields a clear solution with ammonia water. Add 500 parts of distilled water, stir well, and then set the mixture aside to settle. Decant the acid supernatant liquid, and wash the precipitate, first by decantation and afterwards on a filter, until the washings are tasteless. Dry the product by moderate heat.

Reaction.— $\text{BiONO}_3 \cdot \text{H}_2\text{O} + \text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O} = \text{BiC}_6\text{H}_5\text{O}_7 + \text{HNO}_3 + 3\text{H}_2\text{O}.$

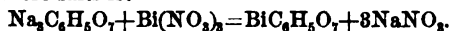
Notes.—Citrate of bismuth is insoluble in water, and nearly so in the dilute nitric acid formed by the reaction taking place in this process. Subnitrate of bismuth is insoluble in ammonia water, but the citrate is soluble in it, and hence the reaction is known to have been completed when the turbid liquid is cleared by ammonia water.

The bismuth citrate is directed to be prepared as follows in the British Pharmacopœia (1885):

Subnitrate of bismuth	22 Gm.
Citric acid	16 Gm.
Sodium bicarbonate	32 Gm.
Nitric acid, 44 C.c., or sufficient.	
Distilled water, sufficient.	

Heat the subnitrate of bismuth with the nitric acid until dissolved. Add a little water, with constant stirring, until the cloudiness produced by the water no longer rapidly disappears. Dissolve the sodium bicarbonate in 480 C.c. of distilled water, add the citric acid, boil until effervescence ceases, and then add this solution to the clear (or only faintly opalescent) solution of nitrate of bismuth until no further precipitate is produced. Heat the mixture to boiling, stirring occasionally. Set aside to cool. When cold, filter, and wash the precipitate until all free nitric acid has been removed. Dry the product by water-bath heat.

Reaction.—Acid bismuth nitrate is formed by the solution of the subnitrate in nitric acid; the citric acid and sodium bicarbonate yield sodium citrate. The reaction between these salts is:



But nitric acid is used in excess, and sodium bicarbonate is also used in excess; and the excess of acid on the one hand is nearly neutralized by the excess of alkali on the other.

CITRATE OF BISMUTH AND AMMONIUM.

BISMUTHI ET AMMONII CITRAS.

Citrate of bismuth	1 part.
Water of ammonia, sufficient.	

Mix the citrate of bismuth with two parts of distilled water to a smooth paste, and gradually add water of ammonia until the salt is dissolved, and the liquid has a neutral or only faintly alkaline reaction. Then filter the solution, evaporate it to a syrupy consistence, spread it on plates of glass, and dry it in scales. Keep the product in small, well stoppered vials, protected from light.

Description.—Small scales, soluble in water and slightly soluble in alcohol. The salt melts without decomposition, but breaks up at a higher temperature.

Tests.—The aqueous solution yields ammonia when boiled with sodium hydrate, or a black precipitate of sulphide when treated with hydrogen sulphide.

BORO-CITRATES.

Several double salts are known, consisting of borates and citrates of potassium, sodium, magnesium, or other metals.

The boro-citrate of potassium is prepared as follows:

BORO-CITRATE OF POTASSIUM.**POTASSII BORO-CITRAS.**

Citric acid.....	10 Gm.
Boric acid	9 Gm.
Potassium carbonate	15 Gm.
Water	60 C.c.

Dissolve and evaporate to dryness, stirring constantly.

MALATES.

The only one used is the extract-like and very impure preparation known as "Extractum Ferri Pomatum," or "Extractum Pomorum Ferratum," official in some pharmacopœias.

MALIC ACID.**ACIDUM MALICUM.**

Potassium malate and malic acid occur in the juice of unripe fruits, as apples, gooseberries, currants, and also in the rhubarb plant.

IMPURE MALATE OF IRON.**EXTRACTUM FERRI POMATUM.**

Iron wire, cut	20 Gm.
Crab apples, nearly ripe	500 Gm.

Pare the apples, beat them into a pulp, and express the juice. Add the iron, mix well, set the mixture in a warm place for ten days, or until all signs of effervescence cease, stirring frequently. Replace from

time to time the water lost by evaporation. Heat the mixture on a water-bath at 70° C. (158° F.) for six hours, replacing water lost by evaporation. Add 100 C.c. of warm water, express, mix the residue with another 100 C.c. of warm water, and express again. Mix the liquids and set the mixture aside in a cool place to settle. Decant the clear liquid, or filter if necessary, and evaporate to a thick extract.

The product is greenish black, has a styptic taste, yields a clear solution with water, and usually contains about 7 to 8 per cent. of iron.

CHAPTER XXVI.

PHENOLS.

PHENYL HYDRATE.

ACIDUM CARBOLICUM.

[PHENOL CARBOLIC ACID.]



Although this substance is not an acid, but an alcohol, it has some properties which resemble those of the acids, and is commonly named carbolic acid. With solutions of the alkalies it forms soluble compounds called phenates, or phenylates, which are capable of dissolving large quantities of phenol. On the addition of an acid to the solution of the phenate, the carbolic acid separates. The solutions of carbolic acid in carbolated soda or potassa are freely miscible with water and alcohol, and are used as disinfectants.

Phenol is one of the many products of the distillation of coal tar. The official "carbolic acid" is a pure phenol obtained by distilling crude carbolic acid between the temperatures of 170° and 185° C. (338° and 365° F.), separating from other products, and purifying by repeated crystallization.

Properties.—Colorless, interlaced, needle-shaped crystals, sometimes acquiring a pinkish tint, deliquescent on exposure, having a distinctive, slightly aromatic odor; when diluted, a sweetish taste, with a slightly burning after-taste, and a neutral reaction. It produces a benumbing, blanching and caustic effect on the skin. The crystals melt at 86° to 42° C. ($96^{\circ}.8$ to $107^{\circ}.6$ F.), and boil at 181° to 186° C. ($357^{\circ}.8$ to $366^{\circ}.8$ F.), the higher melting and the lower boiling points being those of the pure and anhydrous acid. On continued heating, the acid is completely volatilized. Carbolic acid coagulates albumen or collodion (difference from creasote). Its aqueous solution forms a white precipitate with bromine water. On adding to 10 C.c. of a 1 per cent. aqueous solution of carbolic acid, 1 drop of test-solution of ferric chloride, the liquid acquires a violet-blue color which is permanent (the color thus caused by creasote rapidly changing to greenish and brown, with formation, usually, of a brown precipitate). One volume of liquefied carbolic acid, containing 5 per cent. of water, forms, with 1 volume of glycerin, a clear mixture which is not rendered turbid by the addition of 8 volumes of water (absence of creasote and cresylic acid).

The amount of water contained in a solution of carbolic acid may be determined by agitating the solution, in a graduated cylinder, with an equal volume of chloroform. After standing, the upper layer consists of the water contained in the mixture.

Notes.—A carbolic acid having the odor of creasote, or of volatile sulphur compounds, should be rejected. A clean sweet phenol odor is one of the best signs of good quality in carbolic acid. It should also be hard and dry. The variations in the melting and boiling points of phenol are due to the greater or less proportion of water present. An anhydrous acid fused with from four to five per cent. of water will still be a solid mass of crystals at ordinary temperatures; but the phenol is wet in proportion to the amount of water present, and when 8 to 10 per cent. of water is contained in it, the phenol is liquid at ordinary temperatures. The best grades of carbolic acid of the market contain at least 2 and often over 4 per cent. of water. To ascertain approximately the proportion of water, it is most convenient to determine the congealing point of the acid. A thermometer is placed in the melted acid, which is then allowed to cool during constant stirring until it begins to crystallize. The temperature often falls to 5° or 6° C. below the congealing point before crystallization takes place, but the moment this begins the thermometer rises to the true congealing point and remains constant at that point until the crystallization is complete (Squibb). This test is a sensitive one. The best carbolic acid examined by Dr. Squibb congealed at $39^{\circ}.5$ C., and commenced boiling at 170° C., the boiling point rising rapidly at first and more slowly afterwards, until it reached 183° C. Another specimen which congealed at $29^{\circ}.4$ C. began to boil at 173° C., and afterwards reached a stationary boiling point of $186^{\circ}.2$. Dr. Squibb regards the congealing and boiling points given by the Pharmacopœia as too high, and the chloroform test as too unreliable to be of much value. The congealing point should be placed at 35° to 38° C.

The pinkish color which is so frequently met with in carbolic acid is due to such minute quantities of whatever substance causes it, that it has not been conclusively settled what this really is. It has been ascribed to aniline, pyrrhol, rosolic acid, copper, iron, ammonia, etc. This pinkish color is acquired by age, and is most frequently found in the purer and more nearly anhydrous grades. It does not in the least impair the medicinal value of the phenol.

Solubility.—The official statements as to solubility are far from correct. Clear and permanent solutions of water in carbolic acid containing 80 per cent. of phenol have been on the market for several years past, under the name of "Carbolic acid solution No. 1."

According to the official description the crystallized phenol dissolves only 5 per cent. of water, and water dissolves only 5 per cent. of phenol. But crystallized phenol, even when of lower congealing point than that given in the Pharmacopœia, dissolves 86 per cent. of water (Squibb); and water dissolves about 6 per cent. of phenol.

Five parts of phenol dissolve in 1 part of alcohol; 4 parts in 1 part of ether; 8 parts in 1 part of chloroform; 7 parts in 2 parts of glycerin; and 4 parts in 7 parts of olive oil.

Solutions containing any desired proportion of phenol may be made by the use of glycerin, water and alcohol.

Phenol is also soluble in benzol, carbon bisulphide, and fixed and volatile oils.

LIQUID CARBOLIC ACID.**ACIDUM CARBOLICUM LIQUIDUM.**

Crystallized phenol	19 parts.
Distilled water	1 part.

Warm the phenol in a bottle until liquefied; then add the water, and shake well.

Each minim of this solution represents very nearly one grain of crystallized phenol.

CARBOLIC ACID WATER.**AQUA ACIDI CARBOLICI; U. S. P. 1870.**

Crystallized phenol	10 Gm.
Glycerin	40 Gm.
Distilled water, sufficient.	

Triturate the phenol with the glycerin until dissolved; then add enough water to make the whole measure 700 C.c.

GLYCERITE OF CARBOLIC ACID.**GLYCERITUM ACIDI CARBOLICI; U. S. P. 1870.**

Crystallized phenol	100 Gm.
Glycerin	400 C.c.
Mix.	

CAMPHORATED PHENOL.**ACIDUM CARBOLICUM CAMPHORATUM.**

Crystallized phenol	12 Gm.
Camphor	4 Gm.
Distilled water	1 Gm.

Triturate until a homogeneous liquid results.

IODIZED PHENOL.**ACIDUM CARBOLICUM IODATUM.**

Iodine	1 part.
Liquid carbolic acid	4 parts.

Triturate until dissolved, aiding the solution by gentle heat.

CRUDE CARBOLIC ACID.

ACIDUM CARBOLICUM CRUDUM; U. S.

The new "crude carbolie acid" of the Pharmacopœia is a very different thing from the "crude carbolie acid" of the coal tar distillers, which has been an article of commerce under that name for many years. It is important, therefore, to guard against confusion between them.

"Dead oil" is a product of the distillation of coal tar. It contains from 8 to 20 per cent. of mixed phenols. From this "dead oil" is obtained the "crude carbolie acid" of the market, which contains about 50 per cent. of mixed phenols. By distillation of this "crude carbolie acid" the true phenol (crystallizable carbolie acid) is next obtained at between 170° and 185° C. (338° to 365° F.). At 185° C. to 195° C. (365° to 383° F.) the distillation yields a product chiefly consisting of cresol and xylol, but still also containing phenol; this distillate is what the Pharmacopœia of the United States (1880) calls *crude carbolie acid*. It contains at least 90 per cent. of mixed phenols, and usually 94 per cent. In the trade it is called "Impure Carbolie Acid, No. 1." After this second fractional distillate comes a third fraction called "Impure Carbolie Acid, No. 2," containing about 64 per cent. of mixed phenols. The second and third fractions together are designated as "coal tar creasote."

What the present Pharmacopœia calls crude carbolie acid, then, is what is designated in the trade as "Impure Carbolie Acid, No. 1," and contains not less than 90 per cent. of mixed phenols, among which are cresol, phenol and xylol.

When just distilled it is always colorless, but darkens by age until it finally becomes quite dark reddish brown. It has a strong, aromatic, creasote-like odor. It has a benumbing, blanching, and corrosive effect upon the skin or mucous membrane. Its reaction is neutral. With bromine water it gives a flocculent precipitate.

Tests.—Crude carbolie acid should not dissolve in less than 15 parts of water at 15° C. (59° F.), nor should the solution have an alkaline reaction (absence of alkalies).

Mix 50 volumes of the crude carbolie acid, U. S. P., with 1,000 volumes of water in a vessel of the capacity of 2,000 volumes, shake vigorously and then allow it to separate; pour off the upper milky liquid; then add 500 volumes more of water and again shake thoroughly, set aside to separate, and pour off the watery liquid as before. Transfer the residue to a graduated cylinder. The undissolved residue should not measure more than 5 volumes (Squibb).

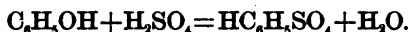
Crude carbolie acid, U. S. P., is a more powerful disinfectant than crystallized phenol. It is intended for free use in hospitals, water-closets, drains, alleys, outhouses, etc.

A crude carbolie acid having an alkaline reaction should always be rejected; alkalies are added to render practicable the dilution of the acid with considerable amounts of water.

An article having a strong odor of sulphur compounds or of ammonia should also be promptly rejected.

SULPHO-CARBOLATES.

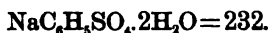
Sulpho-carbolic acid, or orthophenol sulphonic acid, is formed when phenol is digested with sulphuric acid:



Sulpho-carbolates of sodium and zinc are official. The sulpho-carbolates of barium and lead are employed in preparing other sulpho-carbolates by double decomposition with sulphates or carbonates. The salts are colorless, white, or sometimes slightly pinkish, and soluble in water.

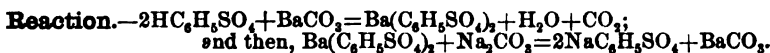
SULPHO-CARBOLATE OF SODIUM.

SODII SULPHO-CARBOLAS.



Crystallized phenol	10 parts.
Sulphuric acid.	12 parts.
Barium carbonate	20 parts.
Sodium carbonate	34 parts.

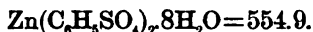
Add the phenol to the sulphuric acid, stir, and heat the mixture on a water-bath for three hours. Add 200 parts of water, and stir well. Then gradually add the barium carbonate, and mix the whole intimately. Filter. Precipitate the filtrate exactly with the sodium carbonate, previously dissolved in 100 parts of water. Again filter, and evaporate to crystallization. Purify the product by re-crystallization until colorless, or but faintly pinkish.



Notes.—Any excess of sulphuric acid present in the sulpho-carbolic acid is removed by the use of an excess of barium carbonate, whereby insoluble barium sulphate is formed, which is filtered away.

Description.—Colorless, transparent, rhombic prisms, permanent in the air, odorless or nearly so, having a cooling, saline, somewhat bitter taste, and a neutral reaction. Soluble in 5 parts of water, and in 133 parts of alcohol at 15° C. (59° F.); in 0.7 part of boiling water and in 10 parts of boiling alcohol. When heated, the salt loses its water and becomes a white powder. At a higher temperature it emits inflammable vapors having the odor of carbolic acid, and leaves a residue amounting to 36 per cent. of the original weight, the filtered solution of which, acidulated with nitric acid, produces a white precipitate with solution of chloride of barium.

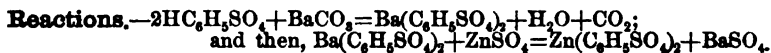
A one per cent. aqueous solution of the salt should not at once be rendered turbid nor be precipitated by solution of chloride of barium (limit of sulphate).

SULPHO-CARBOLATE OF ZINC.**ZINCI SULPHO-CARBOLAS.**

Crystallized phenol.....	20 parts.
Sulphuric acid.....	24 parts.
Barium carbonate.....	40 parts.
Zinc sulphate.....	29 parts.

Add the phenol to the acid, stir, and heat the mixture on a water-bath for three hours. Add 400 parts of water and mix well. Then neutralize by adding the barium carbonate, stirring the whole thoroughly. Filter. Reject the precipitate. To the filtrate add the zinc sulphate previously dissolved in 200 parts of water. Now filter away the precipitated barium sulphate, slightly acidulate the filtrate with sulphuric acid, and evaporate to crystallization.

Purify the product by repeated re-crystallizations.



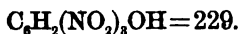
Notes.—The solution of zinc sulphate should be added to the solution of sulpho-carbolate of barium until exactly precipitated—that is, the further addition of zinc sulphate must be discontinued as soon as it no longer causes any further precipitation. Sulpho-carbolate of zinc crystallizes more readily from a solution slightly acidulated with sulphuric acid.

Description.—Thin, colorless plates, soluble in water or alcohol.

Tests.—The aqueous solution is precipitated white by ammonium sulphide, and is colored violet by ferric chloride.

PICRIC ACID.**ACIDUM PICRICUM.**

[TRI-NITRO-PHENOL.]



Tri-nitrophenol, or picric acid, is prepared by dropping 1 part of phenol into 3 parts of warm nitric acid, and then adding, after the violence of the reaction has subsided, 3 parts of fuming nitric acid, and heating the mixture. Upon evaporation the tri-nitrophenol crystallizes. The product is purified by re-crystallization from a hot solution in water or diluted alcohol.

Description.—Lemon yellow crystals, soluble in water and alcohol. The aqueous solution is frequently used as a test for albumen in urine and for alkalis.

SALICYLATES.

The salicylates are recognized by the special test given under Salicylic Acid. The more important of these salts are soluble in water.

SALICYLIC ACID.

ACIDUM SALICYLICUM.

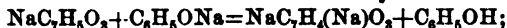


Methyl salicylate exists in the volatile oil of gaultheria, which contains about 90 per cent. of this compound ether. Salicylates have also been found in other plants. Salicylic acid is manufactured as follows:

A solution of sodium hydrate is saturated with phenol, the mixture evaporated to dryness with constant stirring, and the residue, while still hot, is powdered; the powder is heated in a retort over an oil-bath to 100°C . (212°F .) whereby all moisture is driven off; then a current of dry carbonic acid gas is passed into the retort under slight pressure, the temperature being raised to 180°C . (356°F .), and finally to $220^\circ - 250^\circ\text{C}$. ($428^\circ - 482^\circ\text{F}$.). The residue now consists of sodium carbonate and sodium hydrate together with sodium salicylate; it is dissolved in water, and hydrochloric acid is added, by which the salicylic acid is precipitated while sodium chloride remains in solution.

Reactions.— $\text{C}_6\text{H}_5\text{OH} + \text{NaOH} = \text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{O}$; then,
 $\text{C}_6\text{H}_5\text{ONa} + \text{CO}_2 = \text{NaC}_7\text{H}_5\text{O}_3$; and $\text{NaC}_7\text{H}_5\text{O}_3 + \text{HCl} = \text{HC}_7\text{H}_5\text{O}_2 + \text{NaCl}$.

Notes.—Much depends upon a careful regulation of the temperature in this process. Potassium hydrate cannot be used in place of the sodium hydrate, the result being then para-oxy-benzoic acid instead of salicylic acid. The chemical reactions include also the formation of "sodium-salicylate of sodium,"



this compound is decomposed by the HCl yielding salicylic acid and sodium chloride.

The crude salicylic acid is purified and decolorized by filtration of its solution through animal charcoal, and repeated re-crystallization. To perfectly remove the resinous impurities, dialysation is resorted to.

When oil of wintergreen is treated with sodium hydrate and the methyl salicylate of sodium boiled, methyl alcohol and sodium salicylate are formed.

Precipitated salicylic acid (amorphous) is not sufficiently pure for medicinal uses. The crystallized acid is better. Sublimed salicylic acid often has the odor of phenol, and acquires a reddish tint on exposure to air or sun light. The purest acid is that purified by dialysis.

Description.—Fine, white, light, prismatic, needle-shaped crystals, permanent in the air, free from odor of carbolic acid, but sometimes having a slight aromatic odor, of a sweetish and slightly acrid taste and an acid reaction. Soluble in 450 parts of water and in 2.5 parts of alcohol at 15°C .; in 14 parts of boiling water; very soluble in boiling alcohol; also soluble in 2 parts of ether, in 2 parts of absolute alcohol, in 8.5 parts of amyl alcohol, and in 80 parts of chloroform.

When heated to about 175° C. the crystals melt, and at about 200° C. they begin to sublime; at a higher temperature they are volatilized and decomposed with odor of carbolic acid. The aqueous solution is colored intensely violet red by test solution of ferric chloride.

Tests.—A solution of 1 part of salicylic acid in 10 parts of alcohol, mixed with a few drops of nitric acid, should not become turbid upon the addition of a few drops of test solution of nitrate of silver (absence of hydrochloric acid). A saturated solution in absolute alcohol, when allowed to evaporate spontaneously in an atmosphere free from dust, should leave a perfectly white crystalline residue, without a trace of color at the points of the crystals (absence of organic impurities; also of iron). On agitating a portion of salicylic acid with 15 parts of concentrated sulphuric acid, no color should be imparted to the latter within fifteen minutes (foreign organic matter). If 5 C.c. of a saturated aqueous solution of salicylic acid be poured into a test-tube, into which had been introduced, shortly before, a crystal of chlorate of potassium and 2 C.c. of hydrochloric acid, and some water of ammonia be now carefully poured on top, the latter should not assume a reddish or brownish tint (absence of carbolic acid).

SALICYLATED CAMPHOR.

CAMPHORA SALICYLATA.

Camphor	84 parts.
Salicylic acid	65 parts.

Heat together carefully until a solution is formed. Let cool. A crystalline mass is obtained.

SODIUM SALICYLATE.

SODII SALICYLAS.



Salicylic acid	10 parts.
Sodium bicarbonate	6 parts.
Water	40 parts.

Shake the salicylic acid well with the water so as to distribute it uniformly through the liquid. Then add the sodium bicarbonate, a little at a time, shaking well after each addition. Warm the liquid slightly to expel the carbonic acid which is set free. When cold again, filter the solution, and evaporate to dryness, stirring constantly so as to obtain a granulated product. Keep it in well stoppered bottles.



Notes.—It is important that the salicylic acid should be in excess throughout; consequently a small excess of the acid is used, and the sodium bicarbonate added to the acid instead of vice versa. Should the alkali be in excess, the product may become darkened even during the process of manufacture, and never fails to be dark colored when finished or after being kept a short time.

E. Hoffman recommends preparing the salt by stirring 20 parts of sodium bicarbonate and 33 parts of dialyzed salicylic acid with enough water to form a thick paste, allowing the carbonic acid time to escape, and then evaporating to dryness.

The presence of iron, even in minute quantity, colors the preparation and its solutions reddish.

When crystallized from alcohol the salt is in needle-shaped crystals, having the composition shown by the formula given above. At 100° C. (212° F.) it loses its water of crystallization, becoming amorphous and hygroscopic. The salt may absorb as much as 8 per cent. of moisture from the air.

LITHIUM SALICYLATE.

LITHII SALICYLAS.



Salicylic acid	11 parts.
Lithium carbonate	3 parts.
Distilled water	25 parts.

Mix, and heat gently until effervescence ceases. Filter, and evaporate to dryness over a water-bath, stirring constantly. Keep it in well stoppered bottles.



Description.—A white powder, deliquescent on exposure, odorless, faintly acid in reaction, and freely soluble in water and in alcohol.

ZINC SALICYLATE.

ZINCI SALICYLAS.



Zinc oxide	3 parts.
Salicylic acid	10 parts.
Distilled water, sufficient.	

Mix the salicylic acid with 50 parts of water, and heat the mixture. Add gradually the zinc oxide previously mixed with 15 parts of water, until no more dissolves. Filter, and set aside to crystallize.

BISMUTH SALICYLATE

BISMUTHI SALICYLAS.



Prepared by double decomposition from normal bismuth nitrate (59 parts) and sodium salicylate (51 parts). The nitrate of bismuth is dissolved in glycerin, and this solution gradually added to a strong solution of the sodium salicylate in water.

CHAPTER XXVII.

BENZOATES.

The benzoates of sodium, lithium and ammonium are water soluble, and prepared by saturating the acid with the respective carbonates. Benzoate of iron is rarely employed, but useful because soluble in fixed oils.

The solutions of the alkaline salts yield brownish red precipitates with ferric salts, and white precipitates with solutions of lead acetate and silver nitrate.

BENZOIC ACID.

ACIDUM BENZOICUM.



Benzoic acid is contained in benzoin to the extent of from 10 to 19 per cent. and may be obtained by sublimation. The benzoin is coarsely powdered and spread in a thin layer on a flat tinned iron pan. This pan, for one pound of benzoin, ought to be about 12 inches in diameter and about $1\frac{1}{2}$ inches deep. A sheet of porous paper is fastened over the pan, after which a cone or dome of thick paper, which is tied securely around the edges of the pan. The apparatus is then placed on an iron plate, covered with a thin layer of sand. Heat is now applied, gradually, until the odor of benzoic acid becomes quite noticeable through the paper, but the temperature must not be raised too high, for the product will then become fused, or discolored.

Benzoic acid can also be made by the wet way: boiling benzoin with calcium or sodium hydrate, and decomposing the benzoate of calcium or sodium with hydrochloric acid.

Benzoïn..... 4 parts.
Sodium carbonate..... 1 part.
Hydrochloric acid, sufficient.

Digest the benzoin with the sodium carbonate, previously dissolved in 10 parts of water, for three hours at about 60° C. (140° F.). Then boil the mixture a few minutes, filter, and neutralize with hydrochloric acid. Collect the precipitated benzoic acid, and purify it by dissolving it in 20 times its weight of boiling water, digesting the solution with a little animal charcoal, filtering, concentrating the solution by evaporation and crystallizing.

Benzoic acid is now manufactured from hippuric acid, from naphthalin, and from toluol. This artificial benzoic acid is generally pure, chemically, but differs from pure natural benzoic acid by being more compact and almost inodorous. Natural benzoic acid obtained from benzoin by sublimation, is very soft and bulky, and is fragrant. Benzoic acid prepared from benzoin by the wet process is, however, not fragrant. The agreeable odor of sublimed benzoic acid seems to be due to ethyl benzoate, or to some volatile oil, or both, existing in the resin and accompanying the acid when sublimed. The fragrant benzoic acid prepared from benzoin by sublimation is the only kind intended by the Pharmacopœias.

In the trade the natural benzoic acid is styled as "English," and the artificial as "German Benzoic Acid."

Benzoic acid has marked antiseptic properties, and a solution of one part of benzoic acid and one part of borax in 100 parts of water is often employed. The borax aids the solution of the benzoic acid.

Description.—The pure acid crystallizes in colorless, odorless plates. Much of the commercial article has a yellowish tinge. It is readily soluble in alcohol, ether and glycerin, but only slightly soluble in cold water. It should volatilize completely on platinum, and should not reduce potassium permanganate in acid or alkaline solution.

Saturating power.—100 parts of benzoic acid will saturate:

Potassium bicarbonate, 81.97 parts.....	}	Yielding 175.41 parts of potassium benzoate.
Sodium bicarbonate (99 per cent.), 69.55 parts ---		
Sodium carbonate (96 per cent.), 122.09 parts ---	}	Yielding 182.79 parts of sodium benzoate.
Ammonium carbonate, 42.90 parts.....		
Ammonia water (10 per cent.), 139.84 parts	}	Yielding 113.93 parts of ammonium benzoate.
Ammonia water, stronger (28 per cent.), 49.77 parts		

SODIUM BENZOATE.**SODII BENZOAS.**

Benzoic acid	40 parts.
Sodium bicarbonate	28 parts.
Boiling water	80 parts.

Mix the benzoic acid with the hot water, stir well, neutralize perfectly by adding the sodium bicarbonate, being careful to observe the reaction on litmus paper after effervescence has ceased. Filter. Evaporate to 55 parts; remove it from the source of heat and stir until cold. During the evaporation it is necessary to scrape down the benzoate from the sides of the capsule.



Description.—A white, semi-crystalline or amorphous powder, efflorescent on exposure to air, odorless or having a faint odor of benzoin, of a sweetly astringent taste free from bitterness, and having a neutral reaction. Soluble in 1.8 parts of water, and in 45 parts of alcohol at 15° C.; in 1.8 part of boiling water, and in 20 parts of boiling alcohol. When heated, the salt melts, emits vapors having the odor of benzoic acid, then chars and finally leaves a blackened residue of an alkaline reaction, which imparts to a non-luminous flame an intense yellow color, not appearing more than transiently red when observed through a blue glass. On mixing an aqueous solution of the salt with a dilute solution of ferric sulphate, a flesh-colored precipitate is produced.

LITHIUM BENZOATE.**LITHII BENZOAS.**

Lithium carbonate	4 parts.
Benzoic acid	13 parts.
Water	36 parts.

Mix the lithium carbonate and water, heat the mixture in a capsule, and gradually add the benzoic acid until effervescence ceases. Filter, and evaporate to dryness, stirring constantly.



AMMONIUM BENZOATE.**AMMONII BENZOAS.**

Benzoic acid.....	20 parts.
Distilled water.....	40 parts.
Water of ammonia, sufficient.	

Dissolve the benzoic acid in 33 parts of water of ammonia previously diluted with the water. Evaporate over a water-bath by gentle heat, adding a little more ammonia water from time to time, if necessary, to keep the alkali in constant excess, so as to prevent the formation of acid ammonium benzoate, which is less soluble. When reduced to 50 parts set aside to crystallize. Collect and dry the crystals. The mother liquor will yield more crystals after evaporation, keeping the ammonia slightly in excess as before.

**FERRIC BENZOATE.****FERRI BENZOAS.**

To a solution of ferric chloride add ammonia water gradually as long as no precipitate is formed. Then add a solution of ammonium benzoate until precipitation is completed. Collect the precipitate, wash it with a limited amount of cold water, let it drain somewhat, press out the remaining water as far as practicable, and then dry the product without the aid of heat.

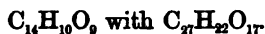
It is a brownish powder, soluble in fixed oils to a limited extent.

CHAPTER XXVIII.

MISCELLANEOUS PREPARATIONS.

TANNIC ACID.

ACIDUM TANNICUM.



Nutgall, in fine powder, ether, each sufficient.

Expose the powdered galls to a damp atmosphere for two or three days, and afterwards add sufficient ether to form a soft paste. Let this stand in a well closed vessel for twenty-four hours. Then, having quickly enveloped it in a linen cloth, submit it to strong pressure in a suitable press, so as to separate the liquid portion. Reduce the pressed cake to powder, mix it with sufficient ether, to which one-sixteenth of its volume of water has been added, to form again a soft paste, and press this as before. Mix the expressed liquids, and expose the mixture to spontaneous evaporation until, by the aid, subsequently, of a little heat, it has acquired the consistence of a soft extract; then place it on earthen plates or dishes, and dry it in a hot air chamber at a temperature not exceeding 100° C. (212° E.).

GLYCERITE OF TANNIN.

GLYCERITUM ACIDI TANNICI.

Tannic acid	5 Gm.
Glycerin	20 C.c.

Mix in a porcelain capsule and heat the mixture on a water-bath, stirring occasionally, until dissolved. The froth which rises to the surface must be removed.

GLYCERITE OF QUERCITANNATE OF LEAD.**GLYCERITUM PLUMBI QUERCITANNATIS.**

Oak bark, in coarse powder.....	175 Gm.
Glycerin	35 Gm.
Solution of subacetate of lead, sufficient.	
Water, sufficient.	

Boil the bark with two liters of water for fifteen minutes. Strain. To the colature add gradually solution of subacetate of lead so long as a precipitate continues to be formed. Collect the precipitate on a wetted muslin strainer and wash it with water until the washings are tasteless. Let drain, and press the magma between bibulous paper until enough of the moisture has been removed from it to reduce its weight to 65 Gm. Mix this while still moist with the glycerin.

BISMUTH TANNATE.**BISMUTHI TANNAS.**

Normal bismuthous nitrate.....	60 Gm.
Glycerin	200 C.c.
Tannic acid.....	27 Gm.
Solution of soda, 240 C.c. or sufficient.	

Triturate the bismuth nitrate to powder; add the glycerin and stir until dissolved; then gradually add solution of soda until a precipitate no longer forms, stirring well; wash the precipitate with distilled water until the washings are tasteless; drain; add the tannic acid to the moist hydrate, mix well, and set aside for two hours, stirring frequently. Then transfer the mixture to a filter, wash with distilled water until the washings are tasteless, and dry the product.

SYRUP OF LIME.**SYRUPUS CALCIS.**

Lime	5 Gm.
Sugar, in coarse powder.....	30 Gm.
Water, sufficient.	

Triturate the lime and sugar thoroughly in a mortar; then add the mixture to 50 C.c. of boiling water, contained in a bright tinned-iron

vessel, and boil for five minutes, constantly stirring. Dilute it with an equal volume of water, and filter through white paper. Finally, evaporate the syrup to 100 Gm.

Notes.—Sugar forms soluble compounds with the oxides of calcium and iron; hence a greater proportion of lime will be contained in this preparation than in lime water. Sugar is, however, decomposed to a certain extent by long boiling with alkalis, and although calcium hydrate does not attack the sugar as energetically as the hydrates of potassium and sodium, the "syrup of lime" is more or less discolored by the decomposition products. The darkening is greater when less sugar is present; hence, the Pharmacopœia directs the use of only a portion of the water during the boiling, the remainder being added afterwards. The boiling should not be prolonged beyond the time stated.

SACCHARATED OXIDE OF IRON.

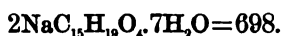
FERRUM OXYDATUM SACCHARATUM SOLUBILE; G.

Solution of ferric chloride (1.281 sp. gr.)	300 Gm.
Sodium carbonate	240 Gm.
Solution of soda (1.16 sp. gr.)	240 Gm.
Sodium bicarbonate	90 Gm.
Sugar	90 Gm.
Sugar, in fine powder, sufficient.	

Dissolve the 90 Gm. of sugar in 90 C.c. of water. Add the solution of ferric chloride. Dissolve the sodium carbonate in twice its weight of boiling water, filter, and let the solution become cold. Then pour the sweetened solution of ferric chloride slowly and with constant stirring into the cold solution of sodium carbonate. After effervescence has ceased, add the solution of soda. When the precipitate has redissolved, add the sodium bicarbonate, immediately followed by 6,000 C.c. of boiling water. Set the mixture aside until the precipitate has subsided perfectly. Then decant the supernatant liquid. Wash the precipitate twice by decantation with boiling water, using 4,000 C.c. each time. Transfer the precipitate to a muslin strainer and continue the washing with hot water until the washings no longer give a decided precipitate with test solution of silver nitrate. Press out the water from the magma as far as practicable. Mix it intimately with 500 Gm. of powdered sugar, dry the mixture in a capsule over a water-bath, and powder it. Then add enough powdered sugar to make the final product weigh 1,000 Gm., and mix well.

Notes.—The ferric hydrate which is first precipitated from the ferric chloride by the sodium carbonate combines with sugar, and the compound formed is soluble in water and in alkaline liquids. The soda solution redissolves it. But as it is insoluble in saline solutions the addition of sodium bicarbonate re-precipitates it. The addition of boiling water, immediately after this re-precipitation, is to render the precipitate denser. The washing is discontinued before all the sodium salt is removed, because otherwise the precipitate would dissolve in the wash water.

The product contains about 3 per cent. of iron.

SODIUM SANTONINATE.**SODII SANTONINAS.**

Santonin.....	100 Gm.
Solution of soda.....	350 Gm.
Water.....	100 Gm.

Mix and digest until dissolved; filter, set in a cool place to crystallize. Evaporate the mother liquor to recover more, as long as the crystals obtained are colorless.

Keep it in a tightly corked bottle, and protected from the light.

Recover the remainder of the santonin from the last mother liquor by acidulating with hydrochloric acid, when it will separate in crystalline form.

ALBUMINATED SANTONINATE OF SODIUM.

Santonin.....	10 Gm.
Sodium bicarbonate.....	40 Gm.
Dry soluble albumen.....	20 Gm.
Water.....	500 C.c.

Digest together at 60° C. (140° F.) until dissolved. Filter. Evaporate by gentle heat. Spread it on glass plates to dry.

Brilliant pearly scales, soluble in water.

PART III.

ANALYTICAL CHEMISTRY.

QUALITATIVE ANALYSIS.

CHAPTER XXIX.

INTRODUCTORY.

In the foregoing chapters the student has become acquainted with important tests for the identification of various common substances; it now remains to show how the several bases and acids of a complex mixture can be detected. It rarely happens in the course of an analysis that an element is separated out as such, but its presence is proven by the appearance of some characteristic compound known to contain it. Silver, for instance, is usually recognized by its *chloride*. If the addition of hydrochloric acid to a solution produces a white *curdy* precipitate, the evidence is pretty strong that silver is present. If this precipitate is insoluble in hot water, and does not blacken on addition of ammonia water, the evidence that it is silver chloride is complete, for the operations just named exclude the chlorides of mercury and lead, which, under certain circumstances, precipitate with silver. No other body behaves in this manner when treated with hydrochloric acid.

Nor is it, as a rule, possible by a qualitative analysis to learn how several bases and acids are combined in a mixture. Tests may prove the presence, in a solution, of copper, zinc, iron, a nitrate, a chloride and a sulphate, but they do not tell us which is the nitrate, which the chloride, or which the sulphate.

In analyzing a mixture many of the tests mentioned above are applied, but to be of service here they must be applied in a certain order. Under the head of Calcium Compounds it was shown that ammonium carbonate

gives, with solutions of calcium salts, a white precipitate, and this was spoken of as a test. But ammonium carbonate gives white precipitates with solutions containing barium, strontium or zinc salts as well, and hence we can regard it as a certain test for calcium only when we know that the metals mentioned (and others) are absent.

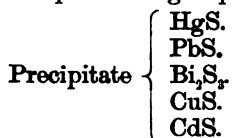
For the purposes of qualitative analysis the metallic elements are divided into groups, which are then further subdivided until special and characteristic tests can be applied for each substance. These groups are purely artificial, and can be compared to the groupings in the analytical key to a system of plant analysis.

Several different classifications have been proposed, and of these the one described in the following pages has been found most generally satisfactory. The principles of this classification can now be explained. Suppose we have a solution containing a large number of elements, and add to it hydrochloric acid in excess; a precipitate forming under these circumstances consists of AgCl , PbCl_2 , or Hg_2Cl_2 , or all of them; and we speak of silver, lead and mercury (in mercurous compounds) as forming a *group*, not because they resemble each other, in general, more than they resemble several other elements, but because in this special instance, and for this special purpose, their behavior is the same. Hydrochloric acid precipitates them, while it does not precipitate other elements. From our complex mixture we have separated, therefore, the *group of insoluble chlorides*, and have



The acid solution from which these are filtered contains other elements, a part of which can be thrown out by adding hydrogen sulphide in excess. Suppose this done, and a precipitate formed and filtered off. This will contain PbS , HgS , Bi_2S_3 , CuS , CdS , As_2S_3 , Sb_2S_3 , and SnS (possibly SnS_2 and Sb_2S_5) if the corresponding metals were present. A small amount of lead sulphide appears here because the chloride as thrown down in the first group, is not absolutely insoluble, and mercury, if present in a *mercuric* salt, precipitates here and not as a chloride. Silver, also, would be thrown down as a sulphide had it not been eliminated before. By the operation just described we have separated another large group from our complex mixture, or, according to the usual classification, *two groups*, as the sulphides of lead, mercury, copper, bismuth and cadmium are readily distinguished from the sulphides of arsenic, antimony and tin by a reaction soon to be explained.

We have, then, the sulphides of group II:



and the sulphides of group III:



We are ready now to separate a *fourth* group from the filtrate after the treatment with H_2S . This can be done by making it alkaline with ammonia water and passing in more H_2S , or by adding ammonium sulphide, which amounts to the same thing. In this way a group of sulphides is obtained from an *alkaline* solution, while before, the sulphides were separated from an *acid* solution. The group so obtained is rather large, and some authors prefer, therefore, a different course.

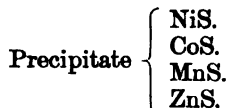
The filtrate is boiled to eliminate the H_2S dissolved in it, treated with a little strong HNO_3 to oxidize certain elements it may contain, and then made alkaline with NH_4OH , in slight excess.

Supposing iron, aluminium and chromium compounds present, the ammonia water would precipitate their hydrates, $\text{Fe}_2(\text{OH})_6$, $\text{Al}_2(\text{OH})_6$, and $\text{Cr}_2(\text{OH})_6$. Under certain circumstances smaller amounts of other substances can precipitate, but this will be explained in its proper place.

We have then the hydrates of group IV:



The alkaline filtrate from these hydrates is next treated with ammonium sulphide, and we obtain—provided nickel, cobalt, manganese and zinc were present in the original mixture—the sulphides of group V:



These sulphides do not precipitate from an *acid* solution; hence they could not appear with the sulphides of the second and third groups.

The filtrate from the last precipitate is treated with a solution of ammonium carbonate, which throws down the carbonates of calcium, barium and strontium, if compounds of these metals are present.

We have then from group VI:



proves the mercury. To prove the arsenic: concentrate the sulphide solution by evaporation, treat it with an excess of nitric acid to decompose the sulphide, then neutralize the acid with sodium carbonate and evaporate to complete dryness. The residue is carefully mixed with a flux containing about equal weights of NaNO_3 and Na_2CO_3 and fused in a porcelain dish or crucible. The mass is allowed to cool, dissolved in water, and neutralized exactly with HNO_3 . Solution of AgNO_3 is now added, which produces a red precipitate of silver arsenate.

We go back now to our first filtrate. This is boiled to remove excess of H_2S , treated with HNO_3 by boiling, to oxidize the iron (however present, iron would be left in the *ferrous* condition by action of the H_2S), and then with a slight excess of NH_4OH and a little NH_4Cl . (This is added here to prevent the precipitation of the magnesium by the ammonia water.) The iron is precipitated as hydrate. This is filtered off, washed, dissolved in HCl , and the solution thus obtained is treated with a few drops of solution of K_4FeCy_6 . A deep blue color proves the iron.

To the filtrate from the iron add $(\text{NH}_4)_2\text{S}$. This precipitates white zinc sulphide. To further prove the zinc, dissolve the precipitate in HCl , evaporate nearly to dryness, take up with water and add solution of K_2CrO_4 . Yellow basic chromate of zinc precipitates.

Concentrate the filtrate from the zinc sulphide, filter off any separated sulphur, add NH_4OH and $(\text{NH}_4)_2\text{CO}_3$, warm and allow to stand. Calcium carbonate precipitates, and after some time can be filtered off. Confirm the calcium by dissolving this in HCl , making slightly alkaline with NH_4OH , and precipitating as oxalate with $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

To find the magnesium, add solution of HNa_2PO_4 to the filtrate from the calcium carbonate. The magnesium separates, usually very slowly, as finely crystalline ammonium-magnesium phosphate, $\text{NH}_4\text{Mg}(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$, NH_4OH and NH_4Cl having been previously added.

Ammonium must be looked for in the original solution. To this end add to a portion of it a little pure KOH or NaOH solution and boil. In the escaping vapor the liberated gas can be recognized by its odor, or by its action on red litmus paper.

A complete analysis would be carried through as just outlined; it would be necessary, in addition, to test for several elements in each group, instead of one.

No satisfactory division of acids into groups can be made, and, as a rule, special tests are employed. These usually follow the tests for metals, and will be given here in that order.

CHAPTER XXX.

ACTUAL ANALYSIS.

A. Preliminary tests. These frequently give the analyst a clew to be followed in the main portion of the work.

- (a). If the substance under examination is a metal or an alloy, its color, density and hardness should be observed.

Very heavy alloys may contain gold or platinum. Aluminium, now frequently used, imparts lightness.

Very white alloys probably contain silver or nickel. Lead, cadmium, antimony, tin and bismuth have a grayish tinge, while gold or copper would be indicated by a yellow or bronze color.

Alloys containing much bismuth or antimony are usually brittle.

If on treatment with strong HNO_3 , the substance does not dissolve, but passes into the condition of a fine insoluble powder, antimony or tin is indicated.

- (b). Closed tube test. Where the substance is solid, but not an alloy, introduce a small portion (powdered) into a closed tube having an internal diameter of 6 Mm. and a length of about 8 Cm. Heat strongly in the flame of a Bunsen burner.

Water may be given off, indicating water of crystallization, mechanically held moisture, or decomposition of organic matter or a complex salt containing O and H.

Gases or vapors may be given off, showing presence of Cl, Br, I, O, CO_2 , SO_2 , etc.

Blackening may occur, indicating the carbonization of organic matter, which is usually accompanied by the evolu-

tion of vapors having a "burnt" odor, or the decomposition of a salt forming a black oxide, as CuO .

A sublimate may form, indicating Hg, As, S, etc.

- (c). Mix a small portion of the powder with an equal weight of dry Na_2CO_3 , then moisten slightly and place in a little cavity scooped in a piece of charcoal. Heat the mass some minutes in the inner blowpipe flame.

By this operation a metallic bead may be produced, from whose physical properties an inference may be drawn.

Cu, Pb, Ag, Au, Sb, Sn, Bi and Cd are reduced in this way, and when alone can often be recognized by the bead.

Sometimes a portion of the metal oxidizes, and thus produces an *incrustation* around the cavity. By the color of this incrustation and its position the presence of certain metals may be indicated.

A few points may be thus tabulated :

Cu.	Au.	Ag.	Pb.	Sn.	Sb.
A red bead somewhat difficult to fuse. Produces yellow alloys with other metals. No incrustation.	A yellow bead, easily malleable, without incrustation.	White malleable bead. No incrustation.	Grayish-white globule with yellow incrustation. Very soft.	White globules, not as readily reduced as Pb; malleable. Incrustation yellowish when hot, white when cold.	Gray brittle globules, which readily oxidize when hot. White incrustation.

B. Solution. As most analytical tests are carried out on solutions, it is an important matter to choose the proper solvent.

Many substances dissolve in water, and where this is possible it is usually the best solvent. Next to water, dilute hydrochloric acid has the preference. Of course, lead, silver and mercurous compounds cannot be brought into solution in this way. Many substances not soluble in dilute hydrochloric acid dissolve in strong, especially when warm.

Where water and hydrochloric acid both fail to effect a solution, nitric acid must be tried.

This is frequently necessary in presence of metals of group I.

Finally, there are a few cases where *aqua regia* must be employed, and here, and in the case above, it is well to remove the excess of acid by evaporation before going on with the regular tests.

In the great majority of practical cases with which the analyst has to deal, water and hydrochloric acid are the only solvents required. Where a portion of a compound is soluble in water and the remainder in hydrochloric acid, it is often best to make two analyses,—one of the water solution, and the other of the acid.

C. Supposing now the solution made by one or the other method, we can proceed with the actual analysis.

CHAPTER XXXI.

ANALYSIS OF GROUP I.*

To a small portion of the solution add a little HCl, if not already present, and shake.

If no precipitate forms pass on to group II. If a precipitate forms add HCl to the whole, shake and allow to stand a short time without heating. Now filter and wash once with cold water. Save the filtrate and washings for the test of group II.

The precipitate on the filter may consist of PbCl_2 , AgCl and Hg_2Cl_2 , and the separation depends on these differences:

- 1°. PbCl_2 , although but slightly soluble in cold water, is completely soluble in hot, while AgCl and Hg_2Cl_2 are insoluble in both.
- 2°. AgCl is soluble in NH_4OH , while Hg_2Cl_2 is not.
- 3°. Hg_2Cl_2 , while not soluble in NH_4OH , is converted by it into another and quite characteristic compound.

Pour boiling water on the filter and repeat this operation several times. The lead chloride dissolves and washes through. It can be detected by concentrating and then cooling the filtrate, when fine needle-shaped crystals appear, or by adding dilute H_2SO_4 , which precipitates the Pb as a fine white powder, PbSO_4 .

* The student can practice on this group with a solution containing AgNO_3 , $\text{Pb}(\text{NO}_3)_2$ and $\text{Hg}_2(\text{NO}_3)_2$.

In case much Pb is present it is best to remove the precipitated chlorides from the filter and boil thoroughly with water, then filter again and wash as before. In this way one can be sure of removing all the $PbCl_2$.

The residue is now treated with moderately strong NH_4OH . This can be done by pouring on the filter, and repeating the operation once or twice. It is not necessary to remove all the $AgCl$ which may be present. To prove the latter, neutralize the NH_4OH filtrate with HNO_3 , when, if it contained $AgCl$, this will be thrown out in the characteristic form.

After the treatment with NH_4OH , Hg_2Cl_2 , if present, would remain as a black compound having the composition of Hg_2ClNH_2 . The Hg in this can be readily shown by drying, mixing it with Na_2CO_3 , and heating the mixture in a closed tube. Hg sublimes and condenses on the colder portions of the glass in characteristic globules.

CHAPTER XXXII.

ANALYSIS OF GROUP II, AND ITS SEPARATION FROM GROUP III.*

Through the filtrate from group I, or the solution in which HCl failed to cause precipitation, pass a current of washed hydrogen sulphide, to complete saturation. If a precipitate forms, allow the gas to bubble through until a clear or nearly clear liquid stands over the subsided sulphides.

Then filter and keep the filtrate for group IV.

Wash the precipitate twice with distilled water, rejecting the washings.

* The student should try the separation of groups II and III with a solution containing $HgCl_2$, $Pb(NO_3)_2$, $Bi(NO_3)_3$, $CuCl_2$, $CdCl_2$, $AsCl_3$, $SnCl_4$, and $SbCl_5$, or other salts which will not precipitate each other. The solution must be dilute.

The precipitate may contain the sulphides of groups II and III; in an extreme case the sulphides of Hg, Pb, Bi, Cu, Cd, As, Sb and Sn.*

The two groups are separated, as explained some pages back, by treatment with $(\text{NH}_4)_2\text{S}$, or with solution of NaSH in certain cases. Boil the precipitate with the $(\text{NH}_4)_2\text{S}$ solution, and filter if a residue is left. The filtrate contains group III, which is taken up in the next chapter. Wash the residue with water, transfer it to a porcelain dish, and boil with dilute HNO_3 .

If everything dissolves, Hg is absent. If a residue remains, Hg may be present as sulphide. By long boiling with HNO_3 , especially if strong, HgS becomes converted into a white but insoluble compound, $2\text{HgS} \cdot \text{Hg}(\text{NO}_3)_2$. This resembles the sulphur usually liberated at the same time, in consequence of which one is often at a loss in affirming the presence of Hg from the appearance of the residue. In any case filter, wash the residue with water, boil it with *aqua regia*, nearly neutralize the solution obtained with a little NH_4OH , and place in it some pieces of bright copper wire or foil. If these become coated with a whitish deposit, the presence of Hg is shown. By drying and heating the copper in a glass tube the Hg is driven off, and collects in droplets above. The residue, insoluble in HNO_3 , may contain some PbSO_4 from the oxidation of PbS , and some SnO_2 from the oxidation of the tin sulphides, as these do not always dissolve readily in $(\text{NH}_4)_2\text{S}$. To detect these metals, use only half the residue for the Hg test, and fuse the other half with a mixture of KCy and Na_2CO_3 . Dissolve the fused mass in water, and if a residue consisting of metallic globules remains, Pb is indicated. A metallic powder remaining would suggest Sn. In either case boil with HNO_3 , and, if anything remains, filter and treat the filtrate with H_2SO_4 for Pb. A white powder on the filter would be metastannic acid.

The filtrate, after the first treatment with HNO_3 , above may contain Pb, Bi, Cu and Cd. To detect them, evaporate off most of the acid, add dilute H_2SO_4 , and allow to stand some hours. If a white precipitate has settled out, it consists of PbSO_4 . Filter it off, and add to the filtrate an excess of NH_4OH . This precipitates Bi, Cu and Cd as hydrates, but redissolves the Cu and Cd. A white flocculent mass remaining consists of BiOOH or BiO_2H_3 —provided lead had been thoroughly separated before addition of NH_4OH .

To confirm Bi, filter this off, dissolve it in a few drops of strong HCl, and pour the solution so obtained into a large quantity of water

*In practice, the color of the precipitate is often a useful indication. If it is a lemon yellow, Cd or As is indicated. An orange yellow indicates Sb, and a brown Sn. In either of these cases the absence of a black color or dirty brownish black is a pretty sure indication of absence of Pb, Cu, Hg or Bi, as the sulphides of these metals are black, and but a small amount is necessary to obscure the yellow or orange sulphides.

in a test-tube. The Bi now precipitates as *orychloride*, BiOCl , milky white.

The presence of Cu would be shown by a deep blue color in the ammoniacal filtrate. To confirm it and find Cd, add $(\text{NH}_4)_2\text{S}$ to precipitate the sulphides. Collect them on a filter, and wash thoroughly with water. Now, without delay, to avoid oxidation of CuS , remove the precipitate from the filter and boil it in dilute H_2SO_4 , 1 volume of acid to 5 of water. An acid of this strength dissolves CdS , but not CuS . Filter, and if $(\text{NH}_4)_2\text{S}$ or H_2S produces a yellow precipitate in the filtrate, the presence of Cd is proven. Dissolve a residue remaining, after treatment with H_2SO_4 , in a little HNO_3 , neutralize this with NH_4OH , and add acetic acid and potassium ferrocyanide solution. A reddish brown precipitate formed consists of copper ferrocyanide, Cu_2FeCy_6 .

CHAPTER XXXIII.

ANALYSIS OF GROUP III.

In the last chapter groups II and III were separated from each other, and the first of these analyzed. We have now to deal with the alkaline sulphide solution, which may contain As_2S_3 , SnS and Sb_2S_3 , in complex combinations as sulphhydrates, as explained among the analytical tests for the metals.

Evaporate it nearly to dryness, add an excess of strong HNO_3 , to decompose the sulphides, and boil. Now neutralize by addition of dry Na_2CO_3 , and evaporate to complete dryness. The mass is next rubbed up with a mixture of equal parts of dry NaNO_3 (not KNO_3) and Na_2CO_3 , and fused, small portions at a time, in a porcelain crucible or dish. This fusion must be conducted very carefully, as the liberated sulphur, and nitrate, acting on each other, may produce unpleasant deflagrations, which sometimes throw portions of the mass out of the crucible. The object of the fusion is to convert the As into soluble sodium arsenate,

Na_3AsO_4 , the Sn into insoluble stannic oxide, SnO_2 , and the Sb into insoluble sodium metantimonate, NaSbO_3 . At a high temperature some of the SnO_2 would form sodium stannate, Na_2SnO_3 , which is soluble in water. Therefore it is necessary to conduct the fusion at the lowest possible temperature. When completed, remove the mass by pouring, or with a glass rod, to a porcelain plate, allow it to cool, then powder it and treat with water. The sodium arsenate dissolves along with the excess of nitrate and carbonate used, and the sulphate formed. Filter, and wash thoroughly with a mixture of alcohol and water. The alcohol is used to prevent solubility of the antimony compound.

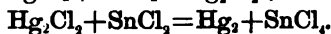
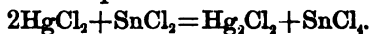
Treat the filtrate, without the alcoholic washings, with a *slight* excess of HNO_3 , and boil. To a portion of the solution add NH_4OH , and then magnesia mixture. The presence of arsenic is shown by the formation of a white crystalline precipitate, $\text{NH}_4\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$.

Another portion of the solution is neutralized with NH_4OH , and then treated with AgNO_3 in excess. If arsenic is present, brick-red silver arsenate, Ag_3AsO_4 , is formed. (This is frequently obscured by AgCl , as chlorides are usually present from some previous operation.) A third portion of the solution may be tested in the Marsh apparatus.

To find Sn and Sb in the residue from the fusion, dissolve it in a little strong HCl , and pour the solution in a Marsh apparatus which has been in operation long enough to expel the air. Light the escaping gas and hold a piece of cold porcelain in the flame. If black spots form, and they are insoluble in solution of bleaching powder, antimony is proven.

If the gas be allowed to pass into a solution of AgNO_3 , a black compound containing silver and antimony, Ag_3Sb , is precipitated. The action in the Marsh apparatus has been explained when treating of metallic antimony and its compounds.

By the action of zinc in the apparatus, tin would be reduced to the state of a metal. To find it, pour off the supernatant liquid, remove any undissolved zinc, and wash any residue remaining with water. Dissolve it in HCl , and add a solution of HgCl_2 . The formation of a white precipitate changing to gray shows the presence of stannous chloride, SnCl_2 . The precipitate consists of Hg_2Cl_2 , mixed with metallic mercury if the SnCl_2 is in excess, and is produced by reduction of HgCl_2 , as shown by these equations:



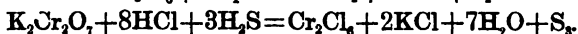
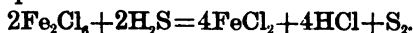
It can be further tested by heating it with NH_4OH , when the black compound described in analyzing group I will be produced.

CHAPTER XXXIV.

ANALYSIS OF GROUP IV.*

The action of hydrogen sulphide on certain compounds of iron and chromium must be explained here, as these metals belong to this group.

If H_2S is passed into an acid solution containing ferric salts, chromates or bichromates, these compounds are *reduced*, the ferric salts to ferrous, and the chromates or bichromates to salts of chromium. These changes may be represented as follows:



The sulphur is separated in both cases in a very finely divided condition, and passes through ordinary filter-paper.

Chromium present as a chromate must therefore be reduced to be found among the metals, and iron, however present, is left as a ferrous salt after the treatment with H_2S .

To go on now with the analysis of group IV:

Boil the filtrate from groups II and III, or the solution in which H_2S has failed to produce a precipitate, until the gas has been driven off, then add a little strong HNO_3 and boil again. This converts the ferrous into a ferric salt, which is necessary for the next process.

NH_4OH is next added in slight excess.

This precipitates group IV completely, as hydrates. It precipitates group V, but redissolves everything excepting a little manganese hydrate, which by the action of the oxygen of the air has become converted into a brownish hydrated peroxide of manganese, insoluble in NH_4OH . We may also have here a precipitate of phosphates, borates or oxalates of the members of group IV, V or VI. These salts, being soluble in acids, remain in solution until the reagent is added to throw down group IV. Neutralization with NH_4OH simply makes

*The student can practice the analysis of group IV with a solution containing the sulphates of iron, aluminium and chromium, a little calcium phosphate dissolved in HCl , and a little manganese sulphate or chloride.

their precipitation possible, and in this way the process becomes somewhat complicated.

Filter, save the filtrate for group V, and wash the precipitate with water. Its color may give an indication of what is present. If pure white, iron and chromium must be absent, aluminium hydrate or some borate, oxalate or phosphate may be present. A red color indicates ferric hydrate, and a greenish chromic hydrate.

If in the analysis of an unknown substance preliminary acid tests have shown the absence of phosphates, borates and oxalates, proceed as follows:

Dry the precipitate and fuse it with a mixture of equal parts of KNO_3 and Na_2CO_3 , using about five parts of the mixture to one of the precipitate, in a small porcelain dish or crucible. By the fusion iron is left as insoluble oxide, chromium is converted into soluble potassium or sodium chromate, K_2CrO_4 or Na_2CrO_4 , aluminium into a soluble aluminate, K_3AlO_3 , and manganese into a soluble manganate, K_2MnO_4 . The color of the fused mass may show what is present, as the chromate is yellow, the aluminate white, the manganate green, and the ferric oxide reddish brown. If more than one is present the colors may be so blended as to give no certain test.

Dissolve the fused mass in water, after cooling, and if a residue remains, filter it off and test a portion of it for iron by dissolving in HCl and adding potassium ferrocyanide, K_4FeCy_6 , which precipitates *Prussian blue*, ferric ferrocyanide, $\text{Fe}_4\text{Cy}_{12}$.

In presence of manganese the filtrate will have a green color sufficient to obscure the pale yellow of the chromate. Divide it into two portions, boil one with acetic acid, and add solution of lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. A yellow precipitate formed consists of lead chromate, PbCrO_4 . A white precipitate of lead sulphate frequently appears here from the presence of sulphates in some of the reagents used.

Acidify the other portion of the filtrate with HCl , add NH_4OH in slight excess, and boil; the formation of a white gelatinous precipitate shows the presence of aluminium.

In presence of phosphates, etc., the following method of separation will generally be found sufficient:

Precipitate with NH_4OH , collect, dry and fuse the precipitate as before.

Digest with water, filter and test the solution for Cr, Mn and Al as before.

Divide the residue into several portions. Treat one of these by dissolving in HCl and adding K_4FeCy_6 , as before, for Fe.

Treat a second portion of the residue with a slight excess of dilute acetic acid by heat, filter and add to the filtrate an excess of $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

A white precipitate appearing now would show presence of Ca, Ba or Sr as oxalates. Dissolve such a precipitate in dilute HCl, and add to the solution some dilute H_2SO_4 . A white precipitate forming now, immediately or on standing, indicates Ba or Sr.

To the filtrate from this, or to the liquid not precipitated by H_2SO_4 , add NH_4OH to alkaline reaction. If this produces a white precipitate Ca is indicated.

The residue from the fusion above may still contain magnesium.

Treat what is left of it with dilute HCl and filter. Add to the filtrate some NH_4Cl and NH_4OH to alkaline reaction. Filter again, and add the filtrate to that to be treated for groups V, VI and VII.

CHAPTER XXXV.

ANALYSIS OF GROUP V.*

Boil the filtrate from group IV, or the solution which has not been precipitated by the reagents of the preceding groups, add to it $(NH_4)_2S$, and boil again thoroughly. This is necessary to bring about complete precipitation.

The precipitate may contain nickel sulphide, NiS , cobalt sulphide, CoS , manganese sulphide, MnS , and zinc sulphide, ZnS . If it is pure white it can contain only ZnS ; if flesh colored it may contain MnS ; if black it must contain either CoS or NiS . (As the latter is not absolutely insoluble in $(NH_4)_2S$, even after boiling, the supernatant liquid generally appears brown when it is present. This shows strongly in the filtrate, and is in itself a good indication.)

Filter and keep the filtrate for group VI. Wash the precipitate with water, remove it from the filter, and treat with cold dilute HCl. This dissolves the sulphides of manganese and zinc, but not those of

* The student can analyze for practice in this group a solution containing the sulphates, nitrates or chlorides of nickel, cobalt, manganese and zinc.

nickel and cobalt. After a time filter again, if a residue remains, and treat the latter in this way:

First, dissolve a little of it in a borax bead. With cobalt this becomes deep blue; with nickel, reddish brown. As one may be obscured by the other it is necessary to make special tests for that not shown by the color. To detect nickel, dissolve the residue in *aqua regia*, evaporate nearly to dryness, and then add strong solution of KCy until a precipitate, formed at first, redissolves. The solution contains now a double cyanide of nickel and potassium, $\text{NiCy}_2 \cdot 2\text{KCy}$, or cobalt and potassium, $\text{CoCy}_2 \cdot 4\text{KCy}$. The latter compound is stable, and if boiled with a solution of a hypochlorite or hypobromite is not reduced, while the former by similar treatment yields black nickelic hydrate, $\text{Ni}_2(\text{OH})_6$. Treat the solution, therefore, with an excess of good NaOCl solution, and boil. A black precipitate proves the nickel.

To find cobalt where the bead shows only nickel: Dissolve the sulphide residue in *aqua regia*, drive off most of the free acid by evaporation, add strong solution of KNO_3 , and then acetic acid in excess. Allow to stand in a warm place. If much cobalt is present it comes down very soon as a yellow precipitate. A small amount may be seen only after hours.

The manganese and zinc possibly contained in the HCl solution are now to be looked for. Boil out the H_2S present, and make alkaline with an excess of NaOH. Both metals would precipitate as hydrates, but the $\text{Zn}(\text{OH})_2$ dissolves in an excess of the precipitant.

If a residue remains filter it off, dry it, and test for manganese by fusing with KNO_3 and Na_2CO_3 . A bluish green color proves it. Test for zinc in the alkaline filtrate by passing into it H_2S after acidifying with acetic acid. A heavy white precipitate proves zinc as sulphide, ZnS . A light precipitate may consist, wholly or in part, of separated sulphur. In such a case it is necessary to apply a special test. Collect the precipitate, dissolve it in HCl, evaporate nearly to dryness, add water, and then solution of K_2CrO_4 . If zinc is present a yellow basic chromate, $\text{Zn}(\text{OH})_2 \cdot \text{ZnCrO}_4 \cdot \text{H}_2\text{O}$, is precipitated.

Zinc can likewise be confirmed in this way: Decompose a little of the sulphide with HNO_3 , evaporate to dryness, and fuse on charcoal with Na_2CO_3 . Now add a drop of $\text{Co}(\text{NO}_3)_2$ solution and fuse again. A green color indicates zinc.

CHAPTER XXXVI.

ANALYSIS OF GROUP VI.*

The filtrate from group V is usually too dilute for the tests of this group. It should, therefore, be evaporated to about one-third its bulk. Sulphur frequently separates by this operation. It should be allowed to settle and then filtered off.

To the filtrate from group V so prepared, or to the solution in which no precipitate has formed by preceding tests, add NH_4OH , NH_4Cl and $(\text{NH}_4)_2\text{CO}_3$. If a precipitate forms it may contain CaCO_3 , BaCO_3 and SrCO_3 . The NH_4Cl prevents the precipitation of MgCO_3 . Filter, keep the filtrate for group VII, and wash the precipitate several times with water. Dissolve it by boiling with acetic acid, add to a small portion of the liquid a solution of $\text{K}_2\text{Cr}_2\text{O}_7$, boil, and allow to stand a short time.

If a precipitate forms treat the whole solution in this way, allow the precipitate to settle, and filter it off. It consists of barium chromate, BaCrO_4 .

To the filtrate add NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ to re-precipitate carbonates free from the $\text{K}_2\text{Cr}_2\text{O}_7$. Filter, if a precipitate forms, and dissolve again in acetic acid. We have now a solution free from barium which may contain calcium and strontium as acetates. Add to this a solution of K_2SO_4 containing about one part to 200 of water. If a precipitate forms after standing it consists of SrSO_4 , as calcium sulphate cannot be thrown down by such a dilute solution. As the precipitate settles very slowly it must be allowed to stand an hour or more before filtering. Finally, pour through a filter, and test the filtrate for calcium by addition of $(\text{NH}_4)_2\text{C}_2\text{O}_4$. A white precipitate formed now consists of calcium oxalate CaC_2O_4 .

Of the several methods proposed for the analysis of this group this seems to give the best results. But certain points must be closely followed.

* Let the student analyze a solution containing the chlorides or nitrates of barium, calcium and strontium.

If barium is present the precipitate of chromate must be thoroughly separated by filtering before testing for the others. The BaCrO_4 is frequently very finely divided, so that it may be necessary to pour back on the filter several times before securing a perfectly clear filtrate.

If $\text{K}_2\text{Cr}_2\text{O}_7$ gives no precipitate with a small portion of the acetic acid solution, it is of course unnecessary to add the reagent to the whole, and in this case the strontium may be tested for directly by adding K_2SO_4 instead.

It occasionally happens that students have difficulty in finding barium, even when known to be present in considerable quantity in the original mixture given for practice in analysis. If the substance must be dissolved in strong nitric acid or *aqua regia*, a portion of the H_2S passed to precipitate groups II and III is oxidized to H_2SO_4 , which throws barium or strontium down in this place. In such cases it is best to search for the metals of group VI, as well as other groups in a solution made with water, or this and HCl .

CHAPTER XXXVII.

ANALYSIS OF GROUP VII.*

The filtrate from group VI, or the solution not precipitated by the preceding group reagents, is divided into two parts. The first, and smaller part, is treated with a solution of NH_4Cl (if sufficient is not already present), NH_4OH and finally some HNa_2PO_4 , and allowed to stand. If magnesium is present it comes down as a fine crystalline precipitate, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$. If the metal is present in small amount only, it comes down very slowly, and it may be necessary to wait several hours for its separation. In any case the precipitate must be crystalline. A flocculent precipitate which sometimes appears here in small amount consists of $\text{Al}_3(\text{PO}_4)_2$. The $\text{Al}_2(\text{OH})_3$ thrown down in group IV is not

*The separation of this group can be practiced with a solution containing MgSO_4 , NH_4Cl , KCl and NaCl .

absolutely insoluble in NH_4OH . The phosphate is less soluble than the hydrate, and consequently when the HNa_2PO_4 is added it produces a precipitate if $\text{Al}_2(\text{OH})_6$ is present.

If magnesium is found it must be eliminated from the larger portion of the filtrate, or solution, reserved for K and Na, before testing for these.

To this end evaporate the solution to dryness in a porcelain dish, and heat it strongly until fuming ceases; that is, until all ammonium salts have been driven off.

Add to the residue pure baryta water to strong alkaline reaction, stir the mixture thoroughly, boil and filter. To the filtrate add NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ in excess, heat to boiling, filter and evaporate this filtrate after addition of a little NH_4Cl to dryness in a dish. Ignite the residue to drive off excess of ammonium salts, allow it to cool, and treat with a few C.c. of water. Filter again, and to one-half the filtrate add a few drops of PtCl_4 solution. If potassium is present in any quantity it comes down as a yellow crystalline precipitate, $\text{PtCl}_4 \cdot 2\text{KCl}$. To find a smaller amount the solution must be evaporated nearly to dryness and a little alcohol added.*

To the other half of the solution add a little fresh solution of potassium metantimonate. If a crystalline precipitate forms, usually after long standing, it consists of sodium metantimonate.

If magnesium is absent the filtrate from group VI can be tested for sodium and potassium by evaporation to dryness, ignition of the residue, and final solution in water, as above. Of course, if nothing remains after the last ignition, no alkalis are present.

The method just explained is excellent provided due attention is given to every point. The test for sodium is certain only when all other salts, except those of potassium, are absent, as they can give somewhat similar precipitates. A simpler method is, therefore, usually followed: The filtrate from group VI, after reserving a portion for magnesium, is evaporated and the residue ignited as before. If anything remains now, treat it with a few drops of water. Dip a platinum wire in this and hold it in the colorless gas flame. If the latter is thereby colored yellow, sodium is present; if violet, the presence of potassium is shown. As a mere trace of sodium can give sufficient color to the flame to obscure a good potassium reaction, it is necessary to observe it through deep blue glass (or an indigo prism), when looking for the latter. The yellow sodium color is in this way shut out, and if violet is present it can be seen. A slight yellow color should not be taken as evidence of the presence of sodium in the original substance, as such a color can be

* If an *iodide* is present, add acid sodium tartrate instead of PtCl_4 .

obtained from the trace of the metal present in most reagents, or in the air, even.

We have still to test for ammonium. Take a portion of the original substance, add to it an excess of strong KOH or NaOH solution, and boil in a test-tube. The presence of NH_3 in the escaping vapor can be detected by its odor, or by means of moistened test-paper. If the latter is used it must be held far enough away from the tube not to be touched by portions of the alkaline *liquid* thrown out by the ebullition.

CHAPTER XXXVIII.

D. TESTS FOR THE ACIDS.

Having found the bases by the methods of the foregoing chapters, we turn now to the detection of the acids with which they were probably combined.

It is not practicable to separate the acids in combination into groups by a process similar to that just given for the metals. As a rule, every acid coming within the scope of this work can be readily found by special tests, such as were given under the discussion of the negative elements. It must be remembered that the results reached in the examination for bases give indications of the presence or absence of certain acids. For instance, chromates, manganates, arsenates or arsenites, would yield chromium, manganese and arsenic among the bases.

Lead, barium or strontium found in a solution exclude anything more than traces of sulphates, as the sulphates of these metals are insoluble in water and acids.

If the substance under examination dissolved in acids without effervescence, it was free from carbonates, sulphites, thiosulphates, cyanides, and sulphides.

Bearing these points in mind, the student can proceed as follows to test for the acids in a compound of unknown origin:

DETECTION OF SULPHATES.

Make a solution of the substance in dilute HCl, or in presence of members of group I, in dilute HNO₃. Filter, if necessary, and treat the filtrate with solution of BaCl₂ or Ba(NO₃)₂. If a white precipitate forms it consists of BaSO₄. This test is sufficient for the detection of sulphates except when originally present as a barium, lead or strontium salt.

DETECTION OF NITRATES.

Dissolve a portion of the original substance in water or dilute H₂SO₄, filter if necessary, and mix the solution with an equal volume of strong H₂SO₄ in a test-tube. Cool it thoroughly, and then pour in carefully, so as not to mix the liquids, a solution of FeSO₄.

In presence of nitrates a brownish ring forms which disappears on shaking the tube, as already described. This test is rendered somewhat uncertain by the presence of iodides, bromides, chromates, manganates and chlorates.

These strong oxygen acids can be reduced by adding to the original solution a sufficient amount of H₂SO₄. After the reduction the excess of this is removed by heat, and if manganates or chromates were present the metals can now be thrown out by boiling with a slight excess of Na₂CO₃.

After filtering, the solution is ready for the ordinary tests.

If bromides or iodides are present they should be eliminated in this way: The filtrate from the above or the original neutral solution free from chlorates, etc., is made slightly acid with acetic acid and treated with an excess of lead peroxide, PbO₂. On boiling, this oxide decomposes bromides and iodides completely, eliminating the bromine and part of the iodine in the free state, and the rest of the latter in the form of lead iodate. When starch paper is no longer colored, the reaction is complete.

The solution is now filtered to separate excess of the peroxide used and iodate formed, and treated with H₂S or H₂SO₄ to separate lead in solution. After filtering, concentrate and test in the usual way.

This method requires considerable time, but gives good results.

DETECTION OF CHLORIDES, BROMIDES AND IODIDES.

Make a solution of a small portion of the original substance in dilute nitric acid, filter if necessary, and add AgNO₃. If no precipitate forms, members of this group are absent. If a precipitate forms,

it may contain AgCl , AgBr and AgI . It is best to apply special tests and not depend on the color of this. Try first the test with MnO_2 and H_2SO_4 , as given in a preceding portion of the work, and if this yields only a greenish yellow gas which has no action on starch paper, chlorine alone is present. In case the gas given off is darker, bromine or iodine, or both, may be present, and as one may obscure the other the method now to be given is recommended.

Boil a portion of the original substance, unless it contains only alkali metals, with solution of Na_2CO_3 , filter, and neutralize the filtrate with dilute H_2SO_4 .

To a portion of the filtrate add solution of CuSO_4 and then an excess of H_2SO_4 . If a dirty white precipitate forms, treat the whole in the same way and filter. The precipitate is cuprous iodide, Cu_2I_2 , and is soluble in ammonia water.

To the filtrate add solution of NaOH sufficient to precipitate the excess of copper, filter again, neutralize with dilute H_2SO_4 , and evaporate to dryness. (If no copper was added, the first solution in Na_2CO_3 could be used, of course.)

Divide the residue into two parts. Dissolve the first in a little water and add chlorine water. The formation of a red color indicates presence of bromine.

Triturate the second portion with some dry $\text{K}_2\text{Cr}_2\text{O}_7$, transfer to a small retort or distilling flask, add strong H_2SO_4 , and apply heat.

If chlorine is present, it distils over as a brownish red gas, chromic oxychloride, CrO_2Cl_2 , which condenses to a red liquid. This treated with excess of NH_4OH yields yellow ammonium chromate $(\text{NH}_4)_2\text{CrO}_4$.

If bromine is present it distils over in the free state, and its solution becomes colorless when treated with excess of NH_4OH .

DETECTION OF CARBONATES, CYANIDES, SULPHITES, SULPHIDES AND THIOSULPHATES.

Treat a small portion of the original substance with HCl . If no effervescence is observed the above salts are absent.

In case of effervescence the odor of the escaping gas may show what is present. Thiosulphates dissolve in HCl , with evolution of SO_2 and deposition of sulphur.

The experiment should be repeated, using more of the substance, in a small flask or test-tube with delivery tube attached. Allow the gas to come into contact with moistened lead paper. If this blackens, the presence of a sulphide is shown.

Pass some of the gas into good clear lime water. If a precipitate forms and redissolves by longer passage of the gas, the presence of a

carbonate is shown. If much SO_2 is present the gas must first pass through solution of $\text{K}_2\text{Cr}_2\text{O}_7$, and then into the lime water.

The odor of sulphurous oxide is usually enough to identify it. In absence of H_2S , allow a little of the escaping gas to act on a mixture of a few drops of Fe_2Cl_6 and $\text{K}_4\text{Fe}_2\text{Cy}_{12}$ solutions.

The appearance of a blue color indicates the reducing action of SO_2 .

This gas is readily absorbed by solution of $\text{K}_2\text{Cr}_2\text{O}_7$, which thereby becomes green, owing to the formation of a chromium salt.

To detect a cyanide, make a solution of the original substance in water or dilute acid, filter if necessary, and add a solution containing a ferrous and a ferric salt. Then add NaOH in excess, and finally, HCl to acid reaction. If a cyanide is present this treatment produces Prussian blue, which shows readily.

The precipitate formed on addition of the NaOH consists mainly of ferrous and ferric hydrates, which must be dissolved by an acid before the blue color can be seen.

DETECTION OF PHOSPHATES.

Make a solution of the original substance in dilute HNO_3 . Filter if necessary, and add an excess of $(\text{NH}_4)_2\text{MoO}_4$ solution. Allow to stand some time in a warm place. If a phosphate is present, it produces a pale yellow crystalline precipitate of ammonium phosphomolybdate, provided enough of the reagent has been added. This reaction is very delicate and characteristic. A yellow color alone is not a sufficient indication of the presence of a phosphate.

The other tests given elsewhere for phosphoric acid are not suitable for its detection in complex mixtures.

DETECTION OF BORATES.

The presence of borates is best shown by treating some of the original substance with strong H_2SO_4 , in amount sufficient to liberate boric acid, and then adding some alcohol. A match is applied, and as the alcohol burns it shows the characteristic greenish yellow color.

By stirring the mixture with a glass rod and withdrawing it from time to time, the alcohol burning on it shows the color very distinctly.

The presence of copper may give a similar reaction. It must be removed by precipitation with H_2S . The evaporated filtrate is then employed for the test.

It is well to make a confirmatory test by means of turmeric paper and the HCl solution of the substance. Boric acid imparts a reddish brown color to turmeric paper.

DETECTION OF FLUORIDES.

Fluorides can be found by mixing some of the original substance with strong H_2SO_4 in a leaden dish, and applying heat.

A piece of glass held over the escaping fumes is etched if a fluoride is present.

This test is seldom necessary.

DETECTION OF CHLORATES.

The reaction with strong H_2SO_4 is a good test. To apply it, carefully add a little of the acid to the substance under examination. The liberation of a greenish yellow gas, accompanied by an explosive noise, indicates a chlorate. Confirm it by converting the chlorate into a chloride by heat and precipitation with AgNO_3 .

If haloids are already present they must be first removed by complete precipitation with the same reagent.

DETECTION OF CHROMATES.

As chromates or bichromates are reduced by H_2S in the test for metals, the change of color of the solution from yellow or reddish yellow to green is a good indication of their presence.

As a confirmatory test, add solution of lead acetate to the aqueous or acetic acid solution of the original substance.

A yellow precipitate of PbCrO_4 proves the presence of a chromate or bichromate.

DETECTION OF ACETATES.

Acetates are most readily found in complex mixtures by adding to the original substance some strong H_2SO_4 and then some alcohol. When heat is applied *ethyl acetate* is formed, which is recognized by its peculiar and pleasant odor. If certain volatile inorganic acids are present they impart at first a sharp odor, but on cooling the presence of the acetate can usually be recognized without difficulty.

DETECTION OF OXALATES AND TARTRATES.

When mixed with inorganic substances these acids are best recognized by boiling some of the original substance with strong solution of Na_2CO_3 . Filter. It may be necessary now, in order to remove certain heavy metals which cannot be precipitated by Na_2CO_3 in presence of organic acids, to treat this filtrate with $(\text{NH}_4)_2\text{S}$. In this case filter again, acidify with HCl , and concentrate by evaporation.

Now make this solution slightly alkaline with NH_4OH , add some NH_4Cl , and finally CaCl_2 solution. Shake thoroughly and allow to stand. If no precipitate forms, tartrates and oxalates are absent.

If a precipitate appears, filter, wash it with water, and finally treat it with a cold solution of NaOH , in which calcium tartrate is soluble. If a residue remains filter again, and boil the filtrate. A gelatinous precipitate appearing now consists of calcium tartrate, $\text{CaC}_4\text{H}_4\text{O}_6$, which can be further identified by filtering, treating with NH_4OH and heating with a crystal of AgNO_3 . If a tartrate is present silver is precipitated as a mirror, on the sides of the tube.

The portion insoluble in NaOH may contain calcium oxalate. Wash it and heat it in a test-tube with strong H_2SO_4 . By this treatment an oxalate is decomposed, giving off CO_2 and CO , the latter of which may be recognized by burning it at the mouth of the tube.

DETECTION OF CITRATES.

A citrate can be identified by several tests. A solution of $\text{Ca}(\text{OH})_2$ added to a solution of a citrate produces at first no precipitate, but on boiling one is thrown down. This reaction distinguishes citrates from tartrates and oxalates, as these salts are decomposed in the cold by solutions of $\text{Ca}(\text{OH})_2$.

The precipitated calcium citrate dissolves partially on cooling.

Alkali citrates are decomposed by solution of $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ with precipitation of amorphous barium citrate. On heating this for some hours on a water-bath it becomes crystalline, and then has the composition $2\text{Ba}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 7\text{H}_2\text{O}$. The crystals are characteristic, and can be best examined by the microscope.

Citrates can be detected in complex mixtures in this way: Proceed as described under oxalates and tartrates. To the solution in which CaCl_2 has failed to produce a precipitate, or, after adding more CaCl_2 , to the filtrate in case of precipitation, add three volumes of strong alcohol. If a precipitate now appears, collect it on a filter, wash with alcohol, and dissolve in HCl . Add NH_4OH to make alkaline, and boil. A white precipitate forming now proves citric acid.

A further discussion of detection of acids is beyond the plan of this work. A few tests have been given in another section for identification of several of the complex organic acids.

It remains now to indicate a process for analyzing several insoluble substances.

CHAPTER XXXIX.

INSOLUBLE COMPOUNDS.

A large number of natural substances and a few artificial products are insoluble in water and acids, and hence remain behind as a residue after preparing the solution for the general examination for bases. We will consider here only the more frequently occurring of these insoluble matters, viz. : *barium sulphate, strontium sulphate, lead sulphate, silver chloride, sulphur, carbon, silica and silicates.*

If a careful preliminary experiment with the blowpipe and charcoal gives no fusible metallic globule, silver and lead need not be looked for here. If, however, a globule was found, then repeat the experiment with a small portion of the residue, and very carefully.

If the result of the fusion with the blowpipe appears doubtful, cut out the surrounding portions of charcoal, powder in a mortar, and treat with water, which will wash away everything light. A metallic residue can now be easily seen. If no such residue remains, lead sulphate and silver chloride may be considered absent.

But when the fusion gives positive evidence of the presence of a metal, these additional tests may be tried: Boil a little of the insoluble substance with strong solution of KCy, and filter, if a residue remains. Add to the solution or filtrate some $(\text{NH}_4)_2\text{S}$. If a dark brown precipitate appears, it shows presence of silver.

If a residue is left after treatment with KCy, it may contain lead sulphate. Wash with water, and if it is white add $(\text{NH}_4)_2\text{S}$ directly to it. Blackening proves the presence of lead. But if the washed residue is black, the lead sulphate possibly contained in it must be extracted by heating with solution of ammonium acetate and acetic acid. The filtrate from this can be tested in the usual way.

Test for sulphur by heating a little of the insoluble substance in a tube closed at one end. If present, characteristic vapors appear.

The presence of charcoal or some form of carbon is indicated by a black color in the insoluble substance. Heat a portion of it very strongly in the air. The carbon will burn off, leaving a light-colored mass.

If the above tests have shown the presence of lead, silver, sulphur or carbon, they must be removed before going farther.

Extract the lead sulphate by means of sufficient ammonium acetate, as above, the silver chloride by treatment with KCy , and eliminate the sulphur or carbon by heating the residue, after treatment for heavy metals.

If anything remains, dry it and proceed as follows:

Mix the residue with 4 parts of dry Na_2CO_3 and 1 part of KNO_3 , and fuse thoroughly in a platinum or porcelain crucible. Allow the mass to cool, and boil out the contents of the crucible with water. Filter, if a residue remains, and wash the latter thoroughly with water. It may contain barium and strontium carbonates, and when washed free from the soluble sulphate, which may have been formed by the fusion, is dissolved in HCl and tested in the usual manner.

Test a portion of the filtrate for H_2SO_4 by acidifying with HCl and adding BaCl_2 .

Acidify another portion with HCl , evaporate to dryness, moisten the residue with HCl , and then add water and boil. If something now remains, it consists of silicic acid. Filter, and examine the filtrate for bases which may have been in combination with the silicic acid. The test for alkalis is, of course, useless, as they were added in the fusing mixture.

SILICATES.

In examining a mineral substance of unknown origin, it is well to evaporate a small portion of the original acid solution to dryness, and redissolve with HCl and water. A silicate partly soluble in acid may have been present, and this treatment would show it. If a residue remains, treat the whole of the solution in the same manner, filter, and use the filtrate for the general tests for bases.

When the substance for examination is known to be a silicate insoluble in acids, reduce it to a fine powder by rubbing in an agate mortar, and fuse sufficient of it in a platinum crucible with the mixture mentioned above, 4 parts of Na_2CO_3 and 1 part of KNO_3 . When the fusion is complete, which is the case when the mass seems to *boil* quietly in the crucible, cool the latter quickly by placing it on a cold iron plate. The contents can then be removed without difficulty. Keep a portion for acid tests, and warm the remainder with dilute

HCl, evaporate to dryness, add water and acid, filter off the separated silica, and use the filtrate for tests for the metals.

To find the alkalies in an insoluble silicate, powder it as before, and heat to bright redness in a platinum crucible for about an hour, with a mixture of 6 parts of pure CaCO_3 and $\frac{3}{4}$ part of powdered NH_4Cl .

The contents should be brought nearly to the fusing point, but not actually fused. When cold, the mass is heated with water for some time and the liquid is filtered. The filtrate contains the alkalies and calcium hydrate and chloride. These are removed by treating with NH_4OH and $(\text{NH}_4)_2\text{CO}_3$, warming and filtering.

The filtrate is evaporated to dryness. The residue is heated strongly to drive off ammonium salts, and then dissolved in water. $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$, in small amount, are added, the solution is filtered and evaporated to dryness again. After igniting it is ready for the application of the tests for alkalies.

This is the best of the several methods proposed for the detection of the alkalies in silicates.

CHAPTER XL.

EXAMINATIONS OF PURE METALS AND ALLOYS.

Heat a small portion, in clippings, or coarse powder preferably, with HNO_3 of 1.2 specific gravity.

If complete solution takes place, gold, platinum, antimony and tin are absent. (Under certain circumstances, traces of platinum and antimony may dissolve in HNO_3 .)

If a residue remains, it may contain gold and platinum in metallic form and tin and antimony as oxides. If the residue is perfectly white, only the last two can be present. Wash with water, keeping the washings apart from the HNO_3 solution, and after drying fuse with a mixture of Na_2CO_3 and NaNO_3 , as in the separation of group III.

Pour the melted mass out, powder it, and treat it with cold water. After a time filter, and wash the residue with alcohol. Test the water filtrate for traces of arsenic which may have been present in the alloy, and which remained insoluble in the treatment with HNO_3 . Heat the residue with dilute HCl , pour in a Marsh apparatus, add some fragments of zinc and platinum foil, add more HCl if necessary, and after a time test the escaping gas for SbH_3 . Examine the platinum foil; if it is colored black the presence of antimony is shown. As a rule, some of the antimony would escape as SbH_3 , while some would come down as a black deposit on the platinum.

After the evolution of hydrogen has ceased, the zinc remaining in excess, remove the latter and wash thoroughly any metallic residue which may be found in the bottom of the flask. It may contain tin, gold and platinum. Boil it with strong HCl , decant the clear liquid from a residue left, if any, and add to it solution of HgCl_2 . A white precipitate proves tin, as in group III.

If antimony has been found, examine a residue insoluble in HCl , by heating first with a little HNO_3 , and $\text{H}_2\text{C}_2\text{H}_3\text{O}_6$. This would dissolve a remaining trace of antimony. If anything is now left, filter, dissolve it in *aqua regia*, and evaporate nearly to dryness. Add solution of KCl and evaporate again. Pour absolute alcohol over the residue, stir thoroughly, and allow to settle. If a yellow precipitate remains, it consists of $\text{PtCl}_4 \cdot 2\text{KCl}$. Filter and wash with alcohol. If the filtrate has a yellow color, gold is indicated. Confirm it by evaporating off the alcohol on a water-bath, dissolving the residue in a little water, and adding a solution of FeSO_4 . Gold precipitates as a very fine brown powder, which remains for a time suspended, imparting a dark blue color to the solution examined by transmitted light.

The HNO_3 solution, in case the alloy was soluble completely, or the filtrate if only partially, must be examined by adding, first, some water. If a milky white precipitate is formed, the presence of bismuth is shown. Add sufficient HNO_3 to dissolve this, and then a little dilute HCl . If a white precipitate now forms, insoluble in HNO_3 , the presence of silver is shown.

The solution can now be further tested as in the general method for the bases, already given.

VOLUMETRIC ANALYSES AND OTHER TESTS.

CHAPTER XLI.

INDICATORS.

The student is already acquainted with the fact that certain organic matters in solution change color when the reaction passes from acid to alkaline or *vice versa*. Some are colorless in acid solution, but highly colored in alkaline. *Litmus* and *phenol-phtalein* are good illustrations. They are very sensitive, a small amount of either being capable of imparting intense color to a beaker of water to which only a trace of alkali has been added.

As employed in analysis, these substances are called *indicators*, and their use is illustrated in this example:

Suppose we have a liter of solution containing exactly 40 Gm. of pure NaOH, and another liter of solution containing 36.4 Gm. of pure HCl. The one would exactly neutralize the other, and any part of the one would neutralize an equal part of the other. One cubic centimeter of the NaOH solution would neutralize 36.4 milligrams of HCl. We can take now a small volume of any dilute hydrochloric acid solution and add to it a few drops of an alcoholic solution of phenol-phtalein. A slight opalescence, only, is produced, Now add gradually from a measuring tube the solution of NaOH, until the colorless acid solution just turns red. This is the *indication* that the neutral point has been reached and slightly overstepped.

If 10 cubic centimeters of alkali have been used, there was present of HCl 364 milligrams. The indicator told us when to stop adding alkali; that is, when just the equivalent of the acid present had been used.

Many other volumetric analyses are made in a manner exactly similar to this, and the same principle, variously modified, is employed

in all. The molecular weight of NaOH is 40, and a solution like the above containing 40 Gm. to the liter is called a *normal* standard solution. One containing 20 Gm. to the liter would be a *half normal* solution, and so on. The solution of HCl contained 36.4 Gm. in a liter. This was likewise a *normal* solution, as 36.4 is the weight of the molecule, HCl.

In general, a number of Gm. equivalent to the molecular weight of a substance dissolved to one liter, makes a normal solution of that substance.

APPARATUS.

In volumetric analysis, various measuring flasks and tubes are employed, the designations and uses of which must now be explained.

Flasks are made to hold a definite volume of liquid when filled to a mark in the neck. The most usual sizes are 1 liter, $\frac{1}{2}$ liter and $\frac{1}{4}$ liter, but other sizes are also sometimes employed. These flasks should have accurately fitted ground glass stoppers.

They are graduated by the manufacturer, and should be tested by weighing them when empty and quite dry, and then when filled to the mark with distilled water, of a known temperature. The increase gives the weight of the water, and when its temperature is known the volume can readily be calculated. Flasks are made to *contain* a definite volume of water or other liquid. (See Fig. 21, F and G.)

Burettes are graduated tubes, as shown in Fig. 21, C, made to *deliver* any desired volume of water or other liquid. They are most readily tested by weighing the amount of distilled water delivered, running out 5 cubic centimeters at a time. For most practical purposes the temperature correction may be disregarded if it is not above 15° C. The usual sizes are 100 C.c., 50 C.c., and 30 C.c., graduated in tenths of 1 C.c.

The lower end is connected by rubber tubing with a delivery tip, and on the rubber is placed a brass pinch-cock to control the flow of the liquid. Better than the pinch-cock is a little glass ball placed inside the rubber tube between the end of the burette and the tip. By pinching the rubber on one side of the ball the liquid is allowed to escape in as fine a stream as is desired.

Pipettes are tubes of the forms shown in Fig. 21, B and D made to *deliver* a definite volume. They are tested by weighing, as before. The usual sizes are 100 C.c., 50 C.c., 25 C.c., 10 C.c., and 5 C.c.

A few other tubes and mixing flasks or jars are sometimes employed, but they need not be described, as their use will be readily seen by the student. At A and E, Fig. 21, a graduated jar and cylinder are shown. It is, of course, understood that a good balance and set of weights must also be at command.

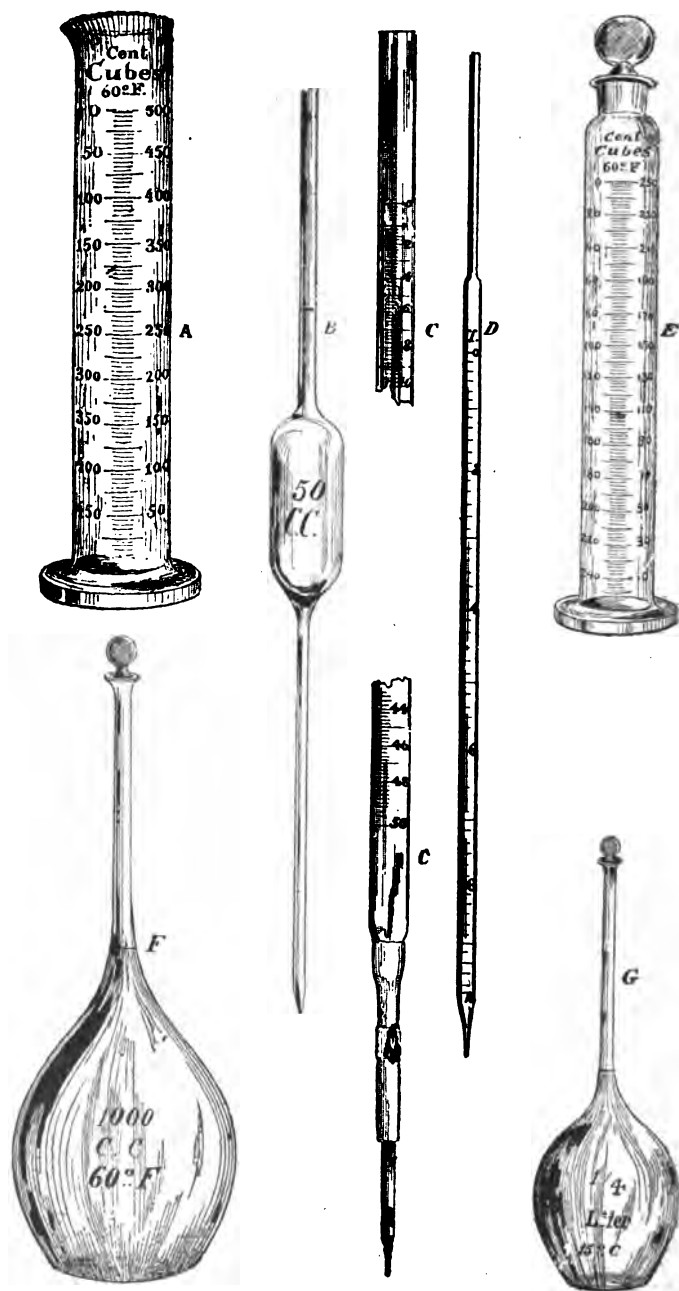


FIG. 21.

SOLUTIONS.

The preparation of an accurate standard solution is a matter requiring very great care. As an illustration we can take first the preparation of half normal sulphuric acid, $\frac{N}{2}$ H_2SO_4 . This contains 49 Gm. of pure H_2SO_4 in a liter.

As the "chemically pure" acid of commerce contains some water, it is necessary to take a quantity somewhat greater than this, say 52 Gm., to the liter. The acid and water are mixed in a beaker, and when cold carefully transferred to a liter flask, which is then filled to the mark and well shaken.

Now prepare a normal sodium hydrate solution, N $NaOH$, by dissolving about 53 Gm. of the pure "stick" soda to a liter.

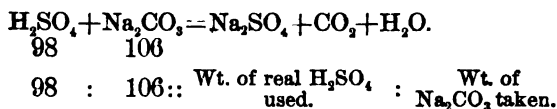
Compare the two solutions in this way: By means of a pipette transfer 25 C.c. of the acid to a beaker, add one or two drops of a weak alcoholic solution of phenol-phtalein, and from a 50 C.c. burette, which has previously been filled with the alkali solution, run in $NaOH$ until, on shaking the beaker thoroughly, a permanent red tinge is obtained. Now repeat the experiment by warming the acid in the beaker and adding *nearly* enough $NaOH$ to color permanently. Place the beaker on a sand-bath and boil for a few minutes, and then add $NaOH$, a drop at a time, until the permanent tinge is reached. This last experiment gives the correct relation of the H_2SO_4 and $NaOH$.

For the 25 C.c. of acid, something less than 25 C.c. of the alkali should be required.

The last test was made in a hot solution, as under these circumstances the phenol-phtalein is more sensitive, not being influenced by the CO_2 of the air, or by that absorbed by the $NaOH$ solution. (After completing the test the liquid in the beaker will *gradually* lose its color. This is due to the action of atmospheric CO_2 , absorbed on cooling, and need not deceive the student.)

Knowing now the relation of the solutions, we proceed to find the absolute value of the H_2SO_4 . Weigh out accurately about two and a half Gm. of pure dry Na_2CO_3 , (made best by igniting the pure washed bicarbonate) and dissolve it in water in a beaker. Add 50 C.c. of the acid, cover quickly with a large watch glass, and when the chief action of the acid has subsided remove it and rinse the drops collected on its under surface into the beaker. Place the latter in a water-bath and warm for a time, then transfer to a sand-bath or gauze and boil out all the liberated CO_2 . Add a little phenol-phtalein, and from the burette run in $NaOH$ to distinct coloration. Observe the number of C.c. used, calculate the acid equivalent to it, and subtract this from the 50 C.c. taken.

This gives the amount used by the Na_2CO_3 , and knowing the weight of this taken, we can find now the strength of the acid by the following relations:



The experiment should be repeated. This is one of the best and most convenient methods of *standardizing* the H_2SO_4 .

When the greatest accuracy is desired, it is best to leave the solution exactly as standardized. It is, however, more convenient for practical work to have it of half normal strength, and this can be made by adding the requisite amount of water to give just 49 Gm. of H_2SO_4 to the liter. In this case 1 cubic centimeter will neutralize the following amounts of alkali:

Potassium hydrate, KOH.....	.0560 Gm.
Sodium hydrate, NaOH	.0400 Gm.
Ammonium hydrate, NH_4OH	.0350 Gm.
Potassium carbonate, K_2CO_3	.0690 Gm.
Sodium carbonate, Na_2CO_3	.0530 Gm.
Sodium carbonate, cryst., $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	.1430 Gm.
Ammonium carbonate, $\text{NH}_4\text{HCO}_3 \cdot \text{NH}_4\text{NH}_2\text{CO}_2$	.0523 Gm.

Having the value of the H_2SO_4 solution, we can determine the strength of the NaOH from this. If it is diluted so as to be just normal, that is, to contain 40 Gm. in a liter, 1 cubic centimeter will be equivalent to the following weights of acid:

Sulphuric acid, H_2SO_4	.0490 Gm.
Hydrochloric acid, HCl.....	.0364 Gm.
Nitric acid, HNO_3	.0630 Gm.
Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	.0630 Gm.
Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$	.0600 Gm.
Citric acid, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$	.0700 Gm.
Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	.0750 Gm.
Potassium bitartrate, $\text{KHC}_4\text{H}_4\text{O}_6$	.1880 Gm.

For certain purposes standard solutions of potassium hydrate and ammonium hydrate may be employed, and instead of sulphuric acid solutions of pure oxalic acid, nitric acid or hydrochloric acid.

The solution of oxalic acid is usually made by weighing the correct amount and dissolving it in water to make a liter of solution.

The solution of hydrochloric acid is made somewhat stronger than necessary, and its exact value determined by precipitation with solution of silver nitrate.

Before giving an illustration of the practical use of these standard solutions, a few words more regarding indicators may be of assistance to the student. A great many of these have been proposed, but litmus and phenol-phtalein will answer all our needs.

Litmus solution is made by treating 10 to 15 Gm. of the powder with 500 C.c. of warm water in a flask, and shaking it frequently during several hours. It is then allowed to settle, when the clear solution may be siphoned or poured off. This is then treated with dilute sulphuric or nitric acid, a drop at a time, until the color changes from blue to violet, that is, until the neutral point is reached. Another drop of acid should be sufficient to color it distinctly red.

The solution must be kept in a loosely stoppered bottle, as it is necessary that the air should have access to it, to prevent decomposition.

As carbonic acid imparts a cherry red color to solutions of litmus it is necessary to expel this gas by heat before making the final *titration*.

Phenol-phtalein can be obtained pure, and for use as an indicator it is simply necessary to dissolve a little in dilute alcohol. One part in a mixture of 200 parts of water and 300 parts of alcohol answers very well. Two or three drops of this solution for 200 C.c. of liquid is sufficient. It cannot be used, however, in presence of any ammonium compound, as its delicacy is thereby very much impaired. It is probable that ammonia and phenol-phtalein unite slowly to form a colorless compound. As already suggested, this indicator is very sensitive to CO_2 , which must be removed by boiling before completing a test.

We can turn now to a few practical illustrations. Let it be required to determine the amount of potassium bitartrate in a sample of "cream of tartar."

Weigh out about 3 Gm., dissolve it in 100 C.c. of hot water, add phenol-phtalein, and then run in from a burette the NaOH solution until a distinct coloration appears. The experiment should then be repeated by dissolving, and adding 1 C.c. less of the NaOH, the phenol-phtalein, and then boiling thoroughly. This will eliminate the small amount of CO_2 introduced by the alkaline solution itself. By adding more from the burette now a slightly smaller quantity will be required than in the first titration. This should be taken as the correct result.

As another illustration, determine the NaOH in commercial "caustic soda."

Dissolve about 2 Gm in 100 C.c. of cold water, add the phenol-phtalein, which strikes immediately a deep color, and run in $\frac{1}{2}$ H_2SO_4 until this color just disappears. If the "caustic soda" were entirely free from carbonate this would be the result required. But some CO_2 is always present, and before the end of the reaction this unites to form HNaCO_3 , which is neutral to phenol-phtalein. By boiling thoroughly

this is decomposed, and the color returns. A little more H_2SO_4 must now be added to complete the reaction, and this additional amount is the equivalent of half the Na_2CO_3 originally present.

If much carbonate is present it must be precipitated out by heating with solution of BaCl_2 . In the filtered liquid the hydrate can be determined by standard solution of HCl .

Other acids and alkalies are determined by exactly similar methods.

In finding the strength of a solution of NH_4OH , litmus must be used as the indicator.

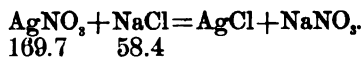
CHAPTER XLII.

ANALYSES BY MEANS OF AgNO_3 .

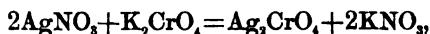
Chlorides, bromides, iodides and several other salts can be readily and accurately determined by standard solution of silver nitrate.

The standard $\frac{N}{10}$ solution is prepared by dissolving 16.97 Gm. of the pure dry crystals to make one liter of solution.

The use of this solution is indicated by the following equation:



The silver nitrate is added in sufficient amount to precipitate all the sodium chloride, and the end point is determined, in neutral solution, by the use of potassium chromate as an indicator. This gives a deep red precipitate with silver nitrate.



but in presence of a chloride a permanent red precipitate of silver chromate cannot form until the chloride is all combined. An illustration will make this clear. Let the student weigh out .584 Gm. of pure dry NaCl and dissolve it in water to make one-fourth liter of solution. 25 C.c. of this are transferred to a beaker, to which one or two drops of a dilute solution of pure K_2CrO_4 are added.

The silver nitrate solution is contained in a burette, and is added, a little at a time, to the contents of the beaker. A heavy white precipitate makes its appearance, and a red precipitate also. But this disappears on agitation. The addition of the AgNO_3 is continued until a faint red color is just permanent. In this case it would be visible on the addition of 10 C.c. of the $\frac{N}{10}$ AgNO_3 .

One cubic centimeter of the solution precipitates the following amounts of several salts:

Sodium chloride, NaCl	.00584 Gm.
Potassium chloride, KCl	.00744 Gm.
Ammonium chloride, NH_4Cl	.00534 Gm.
Sodium bromide, NaBr	.01028 Gm.
Potassium bromide, KBr	.01188 Gm.
Ammonium bromide, NH_4Br	.00978 Gm.
Sodium iodide, NaI	.01496 Gm.
Potassium iodide, KI	.01656 Gm.
Ammonium iodide, NH_4I	.01446 Gm.
Potassium cyanide, KCy	.01300 Gm.

The corresponding acids may be titrated by neutralizing them first with an excess of pure CaCO_3 and filtering.

Special attention must be called to the behavior of cyanides on addition of AgNO_3 .

If one molecule of AgNO_3 be added to two of KCy no precipitate will fall, as a soluble double compound AgCy.KCy is formed. A trace more of AgNO_3 will begin to decompose this with precipitation. The turbidity appears when just one-half the cyanide has been combined, and by multiplying by 2 the number of cubic centimeters of AgNO_3 used to obtain the first trace of a precipitate, we find the amount necessary for the whole.

Another method of estimating chlorides requires the following solutions:

1. $\frac{N}{10}$ AgNO_3 , made as before.
2. $\frac{N}{10}$ NH_4SCy , made by dissolving about 8 Gm. of the pure crystals in a liter, standardizing with the AgNO_3 , and diluting so that they correspond to each other.
3. A strong solution of ammonio-ferric alum, free from chlorine, 50 Gm. to the liter.

To standardize the ammonium sulphocyanate, transfer 25 C.c. of the AgNO_3 to a beaker, add 5 C.c. of the ferric solution, and then pure strong HNO_3 in quantity sufficient to make a colorless solution. Fill the burette with the NH_4SCy and run this slowly into the AgNO_3 . A

white precipitate of AgSCy forms and also a red color, due to the formation of ferric sulphocyanate. This disappears on shaking. However, just as soon as the last portions of silver are combined the next drop of NH_4SCy added strikes a permanent red color, which is the "indication" that enough has been run in to precipitate the silver salt completely. The volume used is now read off, and the solution diluted so as to correspond exactly with the $\frac{N}{10}$ AgNO_3 . To determine a chloride by these solutions proceed as follows:

Add to the solution a measured volume of $\frac{N}{10}$ AgNO_3 , which must be in excess, then the ferric alum and nitric acid as before. We have now AgCl and AgNO_3 , and the problem is to find the latter, which is in excess of that necessary to precipitate all the chlorides. The NH_4SCy combines with the silver salt to form a white precipitate, and with the ferric salt to give it a red color, but the latter is not permanent until the precipitation of the silver is complete. Therefore, the NH_4SCy is run in from a burette until the permanent tinge is obtained, and then the volume added is subtracted from the volume of the silver solution taken. This gives the volume of the $\frac{N}{10}$ AgNO_3 required to combine with the chlorides.

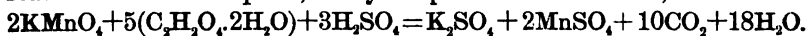
The calculation is the same as before.

Conversely, a standard solution of sodium chloride may be used to determine silver.

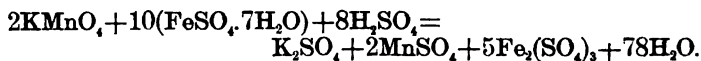
ANALYSES BY MEANS OF KMnO_4 .

Potassium permanganate is a strong oxidizing agent, converting ferrous into ferric salts, oxalic acid into carbon dioxide and water, potassium ferrocyanide into potassium ferricyanide, etc. In these operations the permanganate is reduced to a salt of manganese with complete change of color, and on these facts several valuable processes are based.

A standard solution of permanganate is prepared by dissolving about 5 Gm. of the pure crystals in a liter of water, and comparing the solution with one containing a known amount of iron or oxalic acid. Where pure oxalic acid is at hand, it can be conveniently employed. The reaction which takes place, always in presence of free acid, is this:



Pure ferrous sulphate (by alcohol) gives this reaction:



One molecule of oxalic acid reduces as much permanganate as two molecules of ferrous sulphate.

To make the test by means of iron, weigh out accurately about 2 Gm. of piano wire, previously freed from rust, and cut in small pieces,

and by aid of a gentle heat dissolve it in an excess of pure dilute sulphuric acid contained in a flask. Have the flask fitted with a doubly perforated stopper. Through one passes a glass tube connected with a hydrogen generator, in the other is fitted an open shorter tube. While the iron is dissolving a current of the gas should bubble through the liquid to remove all air. When solution is complete and the lamp has been removed continue the passage of the gas until the liquid is cold. Now dilute it to 250 C.c. with recently boiled out distilled water.

Piano wire contains about .3 per cent. of impurities; we can consider it as .997 pure iron. If 2 Gm. of wire had been taken this would contain 1.994 Gm. of iron.

With a pipette transfer 50 C.c. of the solution, containing .3988 Gm. of iron, to a beaker, add a little water and more dilute H_2SO_4 .

Fill the burette with the permanganate solution and run it into that in the beaker with constant stirring. As long as any of the ferrous salt is present the purple color rapidly disappears; the reaction is complete when a pink tinge persists. If 45 C.c. is necessary for this, 1 C.c. is then equivalent to .008862 Gm. of iron. The experiment should be repeated and the mean of the results taken.

The value of the $KMnO_4$ solution being established it can be used to determine iron in iron salts (ferric salts must first be freed from other acids by treatment with H_2SO_4 , and then reduced with zinc), oxalic acid and oxalates, ferrocyanides and many other compounds.

It is simply necessary to find the relation of the permanganate and the substance in question by an equation similar to those above.

In the titration of oxalic acid and oxalates the liquid must be heated to $60^\circ C.$ after adding the H_2SO_4 and before running in the permanganate.

The calcium in calcium salts, as $CaCl_2$, can readily be determined by this method. The solution is treated with ammonium hydrate, ammonium chloride, and then with an excess of ammonium oxalate. This precipitates calcium oxalate, CaC_2O_4 . The precipitate is allowed to settle, washed as far as possible by decantation, and then *thoroughly* on the filter. While still moist it is transferred to a beaker, and then treated with an excess of dilute H_2SO_4 , which combines with the calcium, liberating a corresponding amount of oxalic acid. The beaker is warmed on a water-bath to $60^\circ C.$, and then the permanganate is added. 40 parts of calcium are equivalent to 126 parts of crystallized oxalic acid or 112 parts of iron.

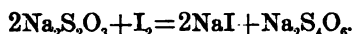
This solution is of great value, especially in the estimation of iron.

The following test is, perhaps, of *wider* applicability:

THE USE OF $\text{Na}_2\text{S}_2\text{O}_3$ AND I.

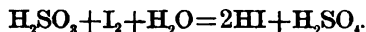
Iodine in presence of water acts as a strong oxidizing agent, and on this fact is based a method of determining a number of reducing substances, and a few oxidizing bodies.

Between iodine and sodium thiosulphate this reaction takes place:



If we have a solution of the thiosulphate and add to it a little thin starch paste, and then run in iodine solution from a burette, a permanent blue will appear only when the $\text{Na}_2\text{S}_2\text{O}_3$ has been completely combined as above.

A very dilute solution of sulphurous acid acts on iodine solution in this way:



In presence of starch paste a blue color would appear only after the complete oxidation of the H_2SO_3 .

The experiment can be tried in another way: Add to the sulphurous acid solution an *excess* of iodine solution, then a little starch paste. Now add $\text{Na}_2\text{S}_2\text{O}_3$ solution from a burette until the blue color just disappears, that is, until the excess of iodine has been combined. If the solutions had been made of a definite strength, it will be seen that the same volume of iodine solution was used to oxidize the sulphurous acid each time.

Upon these principles are founded the following methods of analysis:

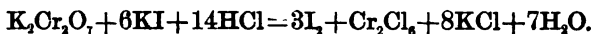
The atomic weight of iodine being 126.6, prepare a decinormal ($\frac{N}{10}$) solution by weighing out carefully 12.66 Gm. of pure sublimed iodine and dissolving it in 150 C.c. of water, containing about 18 Gm. of pure potassium iodide. When solution is complete transfer to a liter flask and dilute with water to the mark. This solution, after thorough mixing, should be poured into two or three small bottles and kept in the dark.

Prepare a $\frac{N}{10}$ $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution by dissolving 24.8 Gm. in water to make one liter. This solution slowly decomposes in the light. It should be kept in a dark cool place.

Make some thin paste by rubbing about 2 Gm. of starch to a cream with a little water, then dilute with 200 C.c. of water and boil. Allow to cool and settle, and then pour off the clear portion. It does not keep well.

With a pipette transfer 50 C.c. of the thiosulphate solution to a beaker, add a little starch, and then from a burette the iodine solution until a blue color just persists. If the solutions are right 50 C.c. of the latter should be necessary to combine with the 50 C.c. of the thiosulphate.

The correctness of the latter can be further tested in this way: Pure solutions of $K_2Cr_2O_7$, KI and HCl act on each other to liberate a definite amount of iodine. This can be taken to standardize the thiosulphate by the usual method.



294 parts of $K_2Cr_2O_7$ liberate 759.6 parts of iodine, or 4.9 Gm. liberate 12.66 Gm., the amount in the $\frac{N}{10}$ I solution.

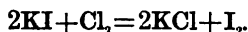
Dissolve 4.9 Gm. of $K_2Cr_2O_7$ in water, make up to one liter. Take 25 C.c. of this solution, and add to it about a Gm. of pure KI in solution, and 5 or 6 C.c. of pure strong HCl in 150 to 200 C.c. of water.

Run in thiosulphate solution until the iodine color has become faint, then add some starch paste and more thiosulphate to complete the reaction.

Just 25 C.c. should be required for this. It is hardly necessary to make this test, if the pure thiosulphate of the leading manufacturers can be obtained, as this substance is made in a state of almost absolute purity, and is quite suitable for a standard.

With our solutions so prepared and tested, a large variety of determinations can be made. The equation given above shows how they may be used in finding the strength of a solution of sulphurous acid.

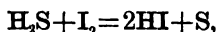
The strength of chlorine water may be determined in this way:



Add to 25 C.c. of the chlorine water an excess of KI solution, and determine the liberated iodine by starch and the thiosulphate.

Or, after the liberation of the iodine, add a known amount of the thiosulphate, but in excess. Then add some starch and iodine solution to coloration. This gives the excess of thiosulphate.

Dilute solutions of H_2S can be determined according to the equation



by adding starch paste, and then the iodine to coloration.

The value of a sample of bleaching-powder can be determined in this way: Weigh out about 10 Gm., rub it to a thin cream with water, dilute to one liter, shake well, and take 25 C.c. of the turbid liquid with a pipette. Transfer this to a beaker, add solution of pure KI in excess, and some HCl to liberate the chlorine of the powder. This is decomposed, an equivalent amount of iodine is set free, which is measured by starch paste, and the thiosulphate in the usual manner.

The strength of "chlorinated soda" solution is determined in an exactly similar manner.

Several other substances are officially tested by the iodine and thiosulphate solutions. The most important of these are given in the next table.

50 C.c. of the iodine solution correspond to:

Acidum arsenosum, with 100 per cent. of As_2O_3 ...	.2475 Gm.
Liquor acidi arsenosi, with 1 per cent. of As_2O_3 ...	24.7500 Gm.
Liquor potassii arsenitis, with 1 per cent. of As_2O_3 ...	24.7500 Gm.
Acidum sulphurosum, with 5 per cent. of SO_2	3.2000 Gm.
Potassii sulphis, with 100 per cent. of $\text{K}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$	.4850 Gm.
Sodii sulphis, with 100 per cent. of $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$	.6300 Gm.
Sodii bisulphis, with 100 per cent. of NaHSO_3 ...	.2600 Gm.

50 C.c. of the thiosulphate solution correspond to the following weights, directly or indirectly (by liberation of iodine):

Aqua chlori, with .5 per cent. of Cl_2	35.400 Gm.
Liquor sodæ chloratæ, with 2 per cent. of Cl_2	8.850 Gm.
Calx chlorata, with 25 per cent. of Cl_2	.708 Gm.
Tinctura iodi, with 8 per cent. of I_2	7.912 Gm.
Liquor iodi compositus, with 5 per cent. of I_2	12.660 Gm.

DETERMINATION OF PHOSPHATES.

Phosphoric acid in solution, free from iron, alumina or much calcium, can be readily determined by solution of uranium acetate or nitrate. Such a solution produces with phosphates a light yellow precipitate of uranium phosphate.

It also gives with potassium ferrocyanide a brownish red precipitate of uranium ferrocyanide. This will form in presence of uranium phosphate, and on this fact is based the use of the potassium ferrocyanide as indicator.

The following solutions are employed:

1. A standard phosphate solution.
This is made by dissolving 10.085 Gm. of pure crystals of sodium phosphate, $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ to make one liter. 50 C.c. of this solution contain .100 Gm. of P_2O_5 .
2. Solution of sodium acetate, containing in one liter 100 Gm. of the acetate and 100 C.c. of 30 per cent. acetic acid.
3. A fresh dilute solution, 1 to 10, of potassium ferrocyanide.
4. A solution of uranium nitrate, made by dissolving about 35 Gm. of the crystallized salt in one liter of water, and standardized as follows:

Transfer 50 C.c. of the phosphate solution to a beaker, add 5 C.c. of the sodium acetate solution, and heat on the water-bath.

Fill a burette with the uranium solution, and by means of a glass rod place a number of drops of the ferrocyanide solution on a white plate.

When the liquid in the beaker is hot run into it the uranium solution from the burette, a few C.c. at a time. Stir well with a rod, and from time to time bring a drop of the liquid in the beaker in contact with one of the drops on the plate. As soon as the reddish precipitate appears stop the titration and begin with a new portion, as this is merely a preliminary test, intended to show about how much of the uranium is needed.

When nearing the final reaction in the second test, add the uranium solution very slowly, and keep the beaker hot. As soon as the lightest red color is imparted to the ferrocyanide by a drop from the beaker the reaction is finished, as the precipitation of the phosphate is complete, leaving any further addition from the burette free to act on the indicator. Repeat the operation, and if the results agree, dilute the uranium solution so that 20 C.c. will be required for the 50 C.c. of sodium phosphate solution, which makes 1 C.c. correspond to .005 Gm. of P_2O_5 .

The solution of uranium nitrate keeps better than one made with the acetate, although the latter would be more convenient in some respects. With the nitrate nitric acid is liberated, but this reacts on the sodium acetate, liberating acetic acid, which does not interfere with the reaction.

With a solution containing no sodium acetate the end reaction is somewhat sharper; but this salt is necessary for the purpose just indicated.

The titration of an unknown solution is performed in a manner exactly similar to that employed in standardizing the uranium solution.

CHAPTER XLIII.

SUGAR ANALYSIS.

Glucose (grape sugar) can be very easily and quickly determined by volumetric analysis. The principle involved in the determination is this, that an alkaline solution of copper sulphate is reduced by solution of glucose, precipitating the copper as red suboxide, Cu_2O . Under definite conditions the amount of copper solution reduced is proportional to the sugar present. The test liquid employed is known as *Fehling's* solution.

The following solutions are prepared:

1. A solution of pure crystals of copper sulphate containing 69.28 Gm. in a liter.
2. A solution containing in one liter 346 Gm. of Rochelle salt and 100 Gm. of pure NaOH. The Rochelle salt should be dissolved in hot water, the solution of NaOH added, and the whole allowed to stand 24 hours. It is then filtered through asbestos, to separate a small precipitate which always appears, and diluted to make one liter, and bottled.

For an experiment, 25 C.c. of each solution is taken, the mixture is brought to boiling in a flask, when from a burette the sugar solution is run in until the deep blue color disappears, leaving only a yellowish-green, showing the complete precipitation of the copper. This is a preliminary test intended to show approximately the amount of sugar present. About 25 C.c. of the sugar solution should be required to reduce the 50 of the mixture, and before making the final test a new solution of sugar should be made having about this strength. Approximately one cubic centimeter of the copper solution is reduced by 5 Mg. of grape sugar. But the reducing power is constant only when the sugar solution contains about one per cent. of glucose, and the first test enables us to fix this with sufficient accuracy.

One C.c. of the Fehling solution is reduced by 4.75 Mg. of glucose in a 1 per cent. solution, and this is the relation to be observed in making the second test.

Mix another 50 C.c. of the Fehling solution and bring it to boiling in a flask. Fill the burette with the approximately 1 per cent. glucose solution and run in, as before, a little at a time, shaking and boiling after each addition. In clear sugar solutions the Cu_2O settles very quickly, so that the disappearance of the blue color can be pretty sharply observed. As the blue fades a green takes its place and when this gives way to a yellowish tinge the reaction is complete. Somewhat greater accuracy can be reached by boiling the copper solution, running in at one time the total amount of sugar thought necessary for reduction, boiling again a few minutes, and filtering quickly. A little of the filtrate acidified with acetic acid and treated with K_4FeCy_6 shows a red color if it still contains copper. Other trials should then be made, using more sugar until the copper test just disappears. If the filtrate from the first test does *not* show copper it is possible that the point has been slightly overreached. In this case a new titration should be made, using slightly less sugar.

In solutions which are not clear this is the best method to follow, as then the disappearance of the blue color can scarcely be observed.

Solutions of *inverted* cane sugar can be tested by this method. The relation to be observed here is: One C.c. of Fehling solution is reduced by 4.94. Mg. of inverted sugar, in a 1 per cent. solution.

Cane sugar can be readily inverted by heating with a little dilute HCl , and then neutralizing exactly with NaOH .

The use of this solution in testing urine will be explained later.

DETERMINATION OF ALCOHOL IN FERMENTED LIQUIDS, BEER, WINE, ETC.

The amount of alcohol in distilled liquors, as whisky, can be easily found by a direct determination of the specific gravity.

In liquors like beer and wine which contain, besides water and alcohol, extractive substances, this method cannot be employed, but one of the following may be used:

1°. *By distillation.* Take 100 to 300 C.c. of the liquid (in weak beers 300, in stronger beers and wines 100 C.c.) measured at a temperature of $15^\circ.5 \text{ C.}$, and distil it in a small retort with Liebig's condenser. Drive over about two-thirds of the liquid, and add distilled water to the distillate so as to bring its volume up to that originally taken, when measured at the same temperature. Determine the specific gravity of this liquid, and from an alcohol table find the corresponding percentage of alcohol.

If the beer or wine taken froths on application of heat, a little tannic acid may be added, which will prevent it.

If the original liquid contains free acid, this should be neutralized by the addition of a little sodium carbonate.

2°. *Indirect method.* This method gives a close approximation, which is sufficient for most practical purposes.

The liquid is gently warmed and shaken to expel carbon dioxide present. 100 C.c. is then measured off and its specific gravity determined, at a definite temperature (15°.5 C.). It is then slowly evaporated on a water-bath until the volume is reduced to 50 C.c. or less. Then cool and add water so as to bring up to the original weight at same temperature, and determine the specific gravity of this.

According to *Bolley* these data can be employed by the following principle:

"The specific gravity of a beer before expulsion of alcohol, is less than the specific gravity of the same after expulsion of alcohol, in the same proportion that the specific gravity of a dilute alcohol of the strength of the beer is less than the specific gravity of water."

As an illustration, suppose the specific gravity of the original liquid free from CO₂ is 1.025; after driving off the alcohol it is 1.034, then:

$$1.034 : 1.025 :: 1 : x (x=.9913).$$

The dilute alcohol, corresponding, has a density, therefore, of .9913. It must contain, from the tables, 5.06 per cent. by weight of alcohol.

There are other methods of calculating the alcohol strength, which can be best seen from the following formulas:

Let a = sp. gr. of original liquid.

b = sp. gr. of alcohol free liquid.

c = per cent. of alcohol corresponding to $\frac{a}{b}$, by weight.

x = per cent. of alcohol in the liquid, by weight.

We have then:

Meyer's formula, $x = c$ corresponding to $1-(b-a)$.

Bolley's formula, $x = c$ corresponding to $\frac{a}{b}$.

Reischauer's formula, $x = \frac{c \text{ corresponding to } \frac{a}{b}}{b}$.

The third formula gives results which are very satisfactory when beer is the liquid tested. The first formula is similar to one proposed by Tabarié for wine, but does not seem to be as accurate as the second.

DETERMINATION OF THE DIASTATIC POWER OF MALT EXTRACT.

The value of the commercial extracts of malt is measured by the amount of *starch* they can convert into *sugar*. In making a test of this it is most convenient to determine the weight of extract necessary to convert 0.1 Gm. of starch into sugar.

Prepare a thin paste by boiling 0.1 Gm. of starch with 100 C.c. of water.

Prepare a solution of the malt extract by dissolving 20 Gm. in a liter of water. Now add 10 C.c. of this solution to the paste, and keep the mixture at a temperature of 60° C. four hours.

Prepare several other starch solutions in the same way, and add to these 20, 30, 40 and 50 C.c. of the extract solution. Heat all of these to 60° C. four hours.

At the end of this time transfer a few drops from each to a white plate, and test with a drop of iodine solution.

In this way it will be found, for instance, that using 20 C.c. of the extract a starch reaction can be obtained, while with 30 C.c. it does not appear. A new experiment should then be made, employing 25 C.c. of the extract, and so on until the starch is just converted.

This method, and in fact any method, of valuation is somewhat empirical, as the element of time is an important factor.

Four hours is recommended, because in that time, practically, all of the conversion possible for a given weight of extract and 0.1 Gm. of starch can be accomplished.

One Gm. of a good extract should convert 0.1 Gm. of starch into sugar in four hours.

Some of the products on the market are much more active than this, while others are almost without effect.

Another test can be made by preparing a paste as above, and adding to it 1.5 Gm. of malt extract in 15 C.c. of water.

The mixture is heated to 60° C. on the water-bath, and at the end of half an hour 5 C.c. is withdrawn with a pipette, cooled, and tested with iodine. If starch is still present, heat longer, and withdraw 5 C.c. every 10 minutes about, and test it. In this way the time necessary for conversion of one part of starch by 15 parts of the extract is determined.

A good extract should not require more than an hour.

ESTIMATION OF TANNIN IN WATER EXTRACTS.

Of the several methods employed for the approximate determination of tannin in vegetable infusions, the following, suggested and perfected

by *Loewenthal*, is, perhaps, the most convenient and reliable. The test is based on the following principles:

A dilute solution of potassium permanganate, acidified with H_2SO_4 , is reduced by solutions of tannin.

The same solution of permanganate is reduced by dilute solutions of indigo-carmin in definite proportion.

Prepare a standard solution of potassium permanganate by dissolving about 1.5 Gm. in a liter of distilled water.

Prepare a standard indigo-carmin solution by dissolving about 30 Gm. of the pure paste, or its equivalent, in a liter of water.

Prepare a solution of pure dry digallic acid (ordinary tannic acid) by dissolving one Gm. in a liter of water.

Determine the relation of these solutions by adding to 1,000 C.c. of water 20 C.c. of the indigo-carmin and 10 C.c. of dilute H_2SO_4 (1 to 5).

The mixture in a beaker is placed on a white ground, and the permanganate solution from a burette added, with constant stirring, until the color of the liquid changes to yellow.

Repeat the experiment by adding to the mixture of water, indigo-carmin and acid, 20 C.c. of the tannic acid solution, and finish as before.

In this test more permanganate will be required than in the first, and the difference expresses that consumed by the 20 C.c. of tannic acid solution.

Repeat the experiment, and if the results agree, dilute the permanganate so that 10 C.c. correspond to 20 C.c. of the tannic acid. The indigo-carmin and permanganate should be exactly equivalent, for convenience.

To obtain the best results in practice, the indigo solution should reduce about $1\frac{1}{2}$ times as much permanganate as the tannin present reduces.

The standard solutions of permanganate and indigo were formerly used directly in the titration of infusions, etc.; but as other substances are always present which have a reducing action, *Loewenthal* recommends to correct the results in this way: A portion of the extract is tested as above, then a second portion is treated with solution of gelatin to precipitate the tannic acid, filtered and tested in the same way. The permanganate now consumed goes to the foreign matters, and is to be subtracted from the results of first test. The details are these:

Prepare a gelatin solution by softening 75 Gm. in water for 24 hours. Then pour off the excess of water and heat the soft mass over a water-bath until it is melted. Add pure sodium chloride to saturation, and finally make up to three liters with saturated salt solution.

Take 100 C.c. of the infusion, add to it 100 C.c. of the gelatin solution, shake thoroughly, and then add 50 C.c. of water, containing 10 C.c. of dilute H_2SO_4 (1 to 5). Allow the mixture to stand some hours and filter. Titrate 50 C.c. of the filtrate with the permanganate as above, and subtract this result from that obtained in the direct titration of 20 C.c. of the infusion. The presence of the gelatin interferes but slightly with the titration, and can usually be neglected.

According to Neubauer .04157 Gm. of digallic acid has the same reducing power as .063 Gm. of oxalic acid. If the permanganate has been standardized by oxalic acid the *weight* of digallic acid in a solution containing this alone can be readily determined.

As the other forms of tannic acid have different reducing powers, calculations based on the above relation would not be correct.

In practice it is best to employ an empirical standard, using high grades of the several materials for comparison.

VALUATION OF JALAP.

Jalap, in fine powder..... 50 Gm.
Alcohol, distilled water, stronger ether, each sufficient.

Moisten the jalap with enough alcohol; set aside in a closed vessel for an hour; pack it firmly in a cylindrical percolator; saturate with alcohol; macerate for forty-eight hours; percolate until the last drops cease to cause any cloudiness on being dropped in water. Evaporate the percolate to 35 C.c., and pour it slowly into 400 C.c. of cold water, with brisk stirring. Collect, wash, dry, and weigh the precipitate.

The precipitate should weigh at least 6 Gm. Shake 1 Gm. of it with 10 C.c. of stronger ether for fifteen minutes in a bottle, pour it out on a tared filter; when it has settled, rinse the bottle thoroughly with some of the clear ethereal solution, adding the rinsings to the mixture on the filter; when the liquid has passed through, wash the residue with a little stronger ether, and then let the filter and contents dry, and weigh them. The net weight of the undissolved resin should be at least 0.90 Gm., showing that the total resin contains not more than 10 per cent. of ether-soluble resin.

TESTING OF PEPSIN.

The official tests to determine the value of pepsin, as given in the United States, British and German Pharmacopœias, differ greatly as to the quantity of water used in proportion to the pepsin and albumen, and the quantity of acid in proportion to water, pepsin, and albumen.

In the Pharmacopœia of the United States, one part of pepsin is suspended in 500 parts of water; in the British Pharmacopœia the proportions are about 1 to 240; and in the German Pharmacopœia, 1 to 1,500.

The proportions between albumen and water are as follows: U. S. P., 1 to 10; B. P., 1 to 4.8; G. P., 1 to 15.

The proportions between pepsin and acid are: U. S. P., 1 to 7.50; B. P. about 1 to 2.50; and the G. P. (reducing the acid to the same strength), as 1 to 1.95.

The proportions between acid and albumen are: U. S. P., 15 to 100; B. P., about 5 to 100; and the G. P., 19.53 to 100.

The proportions between acid and water are: U. S. P., 1.50 to 100; B. P., 1 to 100; G. P., 1.30 to 100.

Besides these differences, the U. S. P. directs that the digestion should be continued 5 or 6 hours; the B. P., only 30 minutes; and the G. P., 4 to 6 hours.

The G. P. directs that the hard-boiled egg albumen should be cut in pieces of the size of lentils; the B. P. directs it to be "passed through a wire gauze of 36 meshes per linear inch, and made of No. 32 brass or copper wire;" whereas the U. S. P. omits to prescribe the state of division of the albumen.

In the U. S. P. the temperature prescribed for this test is 38°—40° C.; in the G. P., 40° C.; and in the B. P., 54° C.

The U. S. P. and B. P. require that 1 part of pepsin should dissolve 50 parts of albumen; the G. P. requires 1 part to dissolve 100 parts.

Most of the pepsin now on the market in the United States probably dissolves more albumen than the U. S. P. demands, by the official test. Many preparations sold as pepsin will be found, when subjected to this test, to dissolve several times as much coagulated egg albumen as demanded by the Pharmacopœia. The "digestive strength" of the preparation is usually indicated on the label, and it is fair that all such preparations should be tested, not by the Pharmacopœial standard, but by the standard given on the label.

For testing pepsin which is labeled U. S. P., or for which no special claim or definite statement of peptogenic power is made, the proper method is that of the Pharmacopœia, which may be carried out as follows:

PROCESS OF THE U. S. PHARMACOPOEIA.

Mix 1.50 Gm. of hydrochloric acid with 500 C.c. of distilled water. This mixture should be made in sufficient quantity for several tests, as it is always best to make more than one test of the same sample; it is referred to below as "acidulated water."

Boil an egg in water for ten minutes. Separate the coagulated albumen, and rub it through a No. 30 wire sieve so as to reduce it to a uniformly fine state of division.

Put 50 C.c. of the acidulated water into a wide-mouthed bottle capable of holding about 200 C.c. Add 0.10 Gm. of the pepsin which is to be tested, and stir well. Then add 5 Gm. of the hard-boiled white of egg, mix well, fasten a paper cap over the mouth of the bottle with a rubber band; set it in a water-bath, and digest at a temperature of 38°—40° C. (100°—104° F.) as long as may be required, not exceeding six hours, stirring the mixture occasionally. A thermometer must be kept in the water-bath throughout, and the temperature carefully controlled. The whole amount of the egg albumen should be dissolved, yielding an almost clear liquid, and the solution is usually accomplished within a much shorter time than the Pharmacopœia allows.

GENERAL METHOD.

Mix 10 Gm. of hydrochloric acid and 1,000 C.c. of distilled water.

Put 100 C.c. of this acidulated water into a wide-mouthed bottle of suitable size; add 0.10 Gm. of the pepsin, and 10 Gm. of the egg-albumen, rubbed through a No. 30 wire sieve; mix well; digest at 40° C. for two hours, stirring occasionally.

Should any portion of the albumen remain undissolved, it may be washed with cold water, drained, and pressed, so as to bring it as nearly to its original condition as practicable, and then weighed, the loss in weight representing the quantity of albumen digested. This, however, is unsafe, and may lead to erroneous conclusions, owing to the difficulty attending the correct estimation of the true amount of the undissolved albumen.

The better plan is to make a series of tests of the pepsin, with different proportions of egg-albumen, until the maximum amount, which the pepsin is capable of converting, has been found.

CHAPTER XLIV.

THE COMMONER ALKALOIDS.

It is intended in this chapter to give tests for the most important of the alkaloids, only. Special works on analysis must be consulted for a discussion of others, and for the methods of detecting and separating them in cases of poisoning.

ALKALOID REAGENTS.

Solutions of several substances precipitate most of the alkaloids from their solutions, and are therefore called *general alkaloid reagents*. The most important of these are:

1. *Picric acid.* Solutions of this acid throw down yellowish precipitates from solutions of nearly all the alkaloids. Most of them are insoluble in excess of dilute H_2SO_4 . Morphine is precipitated only from neutral solutions.
2. *Phospho-molybdic acid.* A solution of this acid in dilute nitric acid is a very delicate reagent, and precipitates all the alkaloids. The precipitates are yellowish or brownish, and when treated with solutions of alkaline hydrates or carbonates are decomposed with separation of the alkaloid.
3. *Double iodide of mercury and potassium.* This solution precipitates most of the alkaloids as whitish flakes.
4. *Iodine in potassium iodide.* The solution used in volumetric analysis gives precipitates with salts of all the alkaloids, which are generally brownish red and flocculent.
5. *Solution of metatungstic acid.* This gives flocculent precipitates with alkaloid solutions, and is an extremely delicate test.

6. *Solutions of mercuric chloride, platinic chloride and auric chloride.* These solutions throw down fine yellowish and white precipitates from solutions of most of the alkaloids.
7. *Solution of tannic acid.* This gives dirty white flocculent precipitates with many alkaloid solutions.

QUININE.

Quinine is found in the market as the free alkaloid, $C_{20}H_{24}N_2O_2 \cdot 3H_2O$, or in the form of a salt, as the sulphate $(C_{20}H_{24}N_2O_2)_2 \cdot H_2SO_4 \cdot 7H_2O$, the bisulphate, $C_{20}H_{24}N_2O_2 \cdot H_2SO_4 \cdot 7H_2O$, and the chloride, $C_{20}H_{24}N_2O_2 \cdot HCl \cdot 2H_2O$.

The solutions of the alkaloid and its salts are very bitter, and may be recognized by these tests:

1°. Free alkalies or alkaline carbonates precipitate quinine as hydrate from solutions of its salts, when not too dilute.

By adding ammonia water and ether to a solution of a quinine salt, the alkaloid is liberated and dissolves, by shaking, in the ether.

2°. If to a solution of a quinine salt, fresh chlorine water is added, and then an excess of ammonia water, a bright emerald-green color is produced.

By adding first chlorine water, then solution of potassium ferrocyanide, and finally the ammonia water, the solution becomes deep red, but the color soon fades.

3°. Solutions of quinine or its salts (excepting the chloride, bromide and iodide) in dilute acids show an azure blue fluorescence. The reaction is best seen when the alkaloid or sulphate is dissolved in dilute sulphuric acid. It is very delicate and characteristic.

4°. Quinine and its salts respond to the tests with most of the alkaloid reagents. Tannic acid solution gives a precipitate with very dilute aqueous solutions of quinine salts.

QUINIDINE.

This alkaloid has the same composition as quinine, but crystallizes with two molecules of water. Salts similar to those of quinine are formed, and many of the reactions obtained from quinine salts can be obtained likewise from those of quinidine. The acid solutions are fluorescent, and the tests with chlorine water, ammonia water and ferrocyanide of potassium are the same as before. These differences may be noted:

1°. It is less soluble in water and in 80 per cent. alcohol than the preceding, but its anhydrous sulphate is easily soluble in chloroform, while quinine sulphate is not.

2°. The hydroiodate obtained by precipitating a neutral solution of the sulphate by a neutral solution of potassium iodide, is only very slightly soluble in water, in which respect it differs from the corresponding quinine compound.

CINCHONINE.

The formula of this alkaloid is $C_{19}H_{22}N_2O$. The crystals are anhydrous; they form alkaline solutions having a bitter taste, and neutralize acids. The following points may be noticed:

1°. Cinchonine is but slightly soluble in ether. Hence if it be liberated from its solution by addition of ammonia water, and ether be then added, the precipitate fails to dissolve, as was the case with quinine.

3°. Acid solutions of cinchonine are not fluorescent.

4°. The addition of chlorine water and then ammonia water to cinchonine solutions produces a white precipitate.

5°. The free alkaloid is very sparingly soluble in water, requiring 3,700 parts for solution. The anhydrous sulphate is readily soluble in chloroform.

CINCHONIDINE.

The formula $C_{19}H_{22}N_2O$ has been given to this alkaloid, like the preceding.

Its solutions are alkaline, and neutralize acids. There are no points specially characteristic of cinchonidine, but the following differences may be noted:

1°. It is but slightly soluble in water, about 1,700 parts being necessary for solution.

The anhydrous sulphate is only sparingly soluble in chloroform.

2°. The acid solutions of cinchonidine are not fluorescent.

3°. Chlorine water and ammonia, and these with potassium ferrocyanide, give no characteristic color reactions with solutions of cinchonidine.

TABLE OF DIFFERENCES.

TEST EMPLOYED.	QUININE.	QUIN- IDINE.	CINCHON- INE.	CINCHON- IDINE.
Action on polarized light.....	—	+	+	—
Solubility in water at 15° C.....	1 g.	1 g.	5 g.	1 g.
Solubility in boiling water.....	1 g.	1 g.	2 g.	—
Solubility in ether.....	1 g.	1 g.	5 g.	1 g.
Solubility in alcohol.....	1 g.	1 g.	1 g.	—
Solubility in chloroform.....	1 g.	—	5 g.	—
Solubility of sulphate in water.....	1 g.	1 g.	1 g.	1 g.
Solubility of sulphate in chloroform.....	1 g.	1 g.	1 g.	1 g.
Solubility of sulphate in alcohol.....	1 g.	1 g.	1 g.	1 g.
Solubility of sulphate in ether.....	nearly insoluble.	nearly insoluble.	nearly insoluble.	nearly insoluble.
Acid solutions.....	fluorescent.	fluorescent.	fluorescent.	fluorescent.
Chlorine water+ammonia water.....	green.	green.	white precipitate.	white precipitate.
Chlorine water+potassium ferrocyan- ide+ammonia water.....	red.	red.	not colored.	not colored.

While it is beyond the scope of this work to go into a full discussion of the many methods proposed for the separation of the cinchona alkaloïds, it will not be out of place to give these approximate tests for the purity of the several commercial products.

1°. *Quinine*. Identified by reactions with chlorine water and ammonia, fluorescence of acid solutions, and by reaction with chlorine water, ammonia and potassium ferrocyanide.

Its purity is determined by the U. S. P. as follows:

“Quinine should afford no color, or none darker than a pale yellow, with undiluted sulphuric acid (abs. of foreign organic matters), nor should it be reddened by nitric acid (difference from morphine). If 1 Gm. of quinine be mixed in a mortar with 0.5 Gm. of sulphate of ammonium and 5 C.c. of distilled water, the mixture thoroughly dried on the water-bath, the residue (which should be neutral to test-paper) agitated with 10 C.c. of distilled water, this mixture macerated at 15° C. (59° F.) for half an hour, then filtered through a small filter, 5 C.c. of the filtrate taken in a test-tube, and 7 C.c. of water of ammonia (sp. gr. 0.980) then added,—on closing the test-tube with the finger and gently turning it until the ammonia is fully intermixed, a clear liquid should be obtained. If the temperature of maceration has been 16° C. (60° 8 F.),

7.5 C.c of the water of ammonia may be added; if 17° C. (62° F.), 8 C.c. may be added. In each instance a clear liquid indicates the absence of more than about 1 per cent. of cinchonidine and quinidine, and of more than traces of cinchonine."

2°. *Quinine sulphate*. (Process of Hesse.) Take .5 Gm. of the sulphate, add 10 C.c. of water at a temperature of 50°–60° C., and shake thoroughly in a test-tube. After ten minutes filter exactly 5 C.c. into a graduated cylinder, add 1 C.c. of ether and 5 drops of ammonia water (strong). Close the graduate with a cork, shake gently and allow to stand two hours. At the end of this time no crystals should be discernible floating in the ether layer. This indicates a satisfactory degree of purity (less than $\frac{1}{4}$ per cent. of cinchonine sulphate, $\frac{1}{2}$ per cent. of quinidine sulphate, or 1 per cent. of cinchonidine sulphate).

If the salt contains $\frac{1}{2}$ per cent. of cinchonine sulphate or 1 per cent. of quinidine sulphate, a precipitate forms in the ether immediately after shaking. If the cinchonidine sulphate present amounts to 3 per cent. or over, a precipitate settles immediately from the ether. 2 per cent. may cause a precipitate after 10 minutes.

The form of the crystals indicates what is present. Crystalline grains are characteristic of cinchonidine, and concentric groups of needles of cinchonine or quinidine.

The following is the process of the U. S. P.:

If one Gm., previously dried at 100° C. (212° F.), be agitated with 10 C.c. of distilled water, the mixture macerated at 15° C. (59° F.) for half an hour, then filtered through a small filter, 5 C.c. of the filtrate taken in a test-tube, and 7 C.c. of water of ammonia (sp. gr. 0.980) then added,—on closing the test-tube with the finger and gently turning it until the ammonia is fully intermixed, a clear liquid should be obtained. If the temperature of maceration has been 16° C. (60° F.), 7.5 C.c. of the water of ammonia may be added; if 17° C. (62° F.), 8 C.c. may be added. In each instance a clear liquid indicates the absence of more than about 1 per cent. of cinchonidine or quinidine, and of more than traces of cinchonine.

3°. *Quinidine sulphate*. The test given by Hesse (followed by the U. S. P.) is this:

.5 Gm. of the salt and .5 Gm. of purest potassium iodide are treated with 10 C.c. of water at a temperature of about 60° C., in a test-tube, which is well shaken. After an hour filter and add to the filtrate a drop of ammonia water. No precipitate should form, showing absence of quinine, cinchonine and cinchonidine.

4°. *Cinchonine sulphate*. The solution in dilute sulphuric acid should show no fluorescence, indicating absence of quinine or quinidine.

Chlorine water and ammonia should give no green color. Dry 1 Gm. of the salt, place it in a test-tube, add 70 Gm. of chloroform, and shake frequently through an hour.

It should dissolve completely, a residue remaining indicating small amounts of quinine or cinchonidine.

5°. *Cinchonidine sulphate*. The solution in dilute sulphuric acid should not be fluorescent.

A green color should not be produced by addition of chlorine water and ammonia.

The salt treated with solution of potassium-sodium tartrate yields a white crystalline precipitate of cinchonidine tartrate, which is insoluble in excess. This is the basis of a test.

Treat .5 Gm. of the salt with 20 C.c. of cold distilled water, and add .5 Gm. of the Rochelle salt. The mixture is kept at a temperature of about 15° C., and shaken frequently through an hour. Filter, and to the filtrate add one or two drops of ammonia water. Nothing more than a slight turbidity should appear. This turbidity would occur in presence of small amounts of cinchonine or quinidine sulphate.

ASSAY OF CINCHONA BARK.

(U. S. P.)

I. *For Total Alkaloids.*

Cinchona, in No. 80 powder, and fully dried at 100° C. (212° F.).....	20 Gm.
Lime.....	5 Gm.
Diluted sulphuric acid, solution of soda, alcohol,	
Distilled water, each, sufficient.	

Make the lime into a milk with 50 C.c. of distilled water, thoroughly mix therewith the cinchona, and dry the mixture completely at a temperature not above 80° C. (176° F.). Digest the dried mixture with 200 C.c. of alcohol, in a flask, near the temperature of boiling, for an hour. When cool, pour the mixture upon a filter of about six inches (15 centimeters) diameter. Rinse the flask and wash the filter with 200 C.c. of alcohol, used in several portions, letting the filter drain after use of each portion. To the filtered liquid add enough diluted sulphuric acid to render the liquid acid to test-paper. Let any resulting precipitate (sulphate of calcium) subside; then decant the liquid, in portions, upon a very small filter, and wash the residue and filter with small portions of alcohol. Distil or evaporate the filtrate to expel all the alcohol, cool, pass through a small filter, and wash the latter with

distilled water slightly acidulated with diluted sulphuric acid, until the washings are no longer made turbid by solution of soda. To the filtered liquid, concentrated to the volume of about 50 C.c., when nearly cool, add enough solution of soda to render it strongly alkaline. Collect the precipitate on a wetted filter, let it drain, and wash it with small portions of distilled water (using as little as possible), until the washings give but a slight turbidity with test-solution of chloride of barium. Drain the filter by laying it upon blotting or filter paper until it is nearly dry.

Detach the precipitate carefully from the filter and transfer it to a weighed capsule, wash the filter with distilled water acidulated with diluted sulphuric acid, make the filtrate alkaline by solution of soda, and, if a precipitate result, wash it on a very small filter, let it drain well and transfer it to the capsule. Dry the contents of the latter at 100° C. (212° F.) to a constant weight, cool it in a desiccator and weigh. The number of Gm. multiplied by *five* equals the percentage of total alkaloids in the cinchona.

II. For Quinine.

To the total alkaloids from 20 Gm. of cinchona, previously weighed, add distilled water acidulated with diluted sulphuric acid, until the mixture remains for ten or fifteen minutes after digestion, just distinctly acid to test-paper. Transfer to a weighed beaker, rinsing with distilled water, and adding of this enough to make the whole weigh *seventy times* the weight of the alkaloids. Add now, in drops, solution of soda previously well diluted with distilled water, until the mixture is exactly neutral to test-paper. Digest at 60° C. (140° F.), for five minutes, then cool to 15° C. (59° F.) and maintain at this temperature for half an hour. If crystals do not appear in the glass vessel, the total alkaloids do not contain quinine in quantity over *eight per cent.* of their weight (corresponding to *nine per cent.* of sulphate of quinine, crystallized). If crystals appear in the mixture, pass the latter through a filter not larger than necessary, prepared by drying two filter papers of two to three and a half inches (5 to 9 centimeters) diameter, trimming them to an equal weight, folding them separately, and placing one within the other so as to make a plain filter four-fold on each side. When the liquid has drained away, wash the filter and contents with distilled water of a temperature of 15° C. (59° F.), added in small portions, until the entire filtered liquid weighs *ninety times* the weight of the alkaloids taken. Dry the filter, without separating its folds, at 60° C. (140° F.), to a constant weight, cool, and weigh the inner filter and contents, taking the outer filter for a counter-weight. To the weight of effloresced sulphate of quinine so obtained, add 11.5 per cent. of its amount (for water of

crystallization), and add 0.22 per cent. of the weight of the entire filtered liquid (for solubility of the crystals at 15° C.). The sum in Gm., multiplied by *five*, equals the percentage of crystallized sulphate of quinine equivalent to the quinine in the cinchona.

MORPHINE.

Morphine, the most valuable constituent of opium, has the composition $C_{17}H_{19}NO_3$. It is bitter and but slightly soluble in water. More readily soluble in alcohol. The solutions are alkaline.

Among the many tests by which it may be recognized the following are perhaps the best:

1°. A neutral solution of ferric chloride, added to a neutral morphine salt, or to a strong solution, produces a deep blue color.

2°. Nitric acid gives a yellowish-red color with strong solutions of morphine. The color is not changed to violet on addition of stannous chloride (difference from brucine).

3°. A solution of five milligrams of ammonium molybdate in 1 C.c. of strong sulphuric acid gives with morphine salts a reddish-violet color. This color gradually changes to greenish-brown, and finally to deep blue, by oxidation from the air.

The test is best carried out in a porcelain dish. The three colors referred to must appear in the order given. The blue color alone is without significance, as many other organic substances produce it with the reagent.

4°. Morphine and its salts dissolve, when gently warmed, in strong sulphuric acid.

If, after cooling this solution, a few drops of sulphuric acid (10-15), containing a little nitric acid, be added, and then two or three drops of water, a violet-red color is produced.

If now some manganese dioxide be added, and stirred in with a rod, a mahogany color will be obtained.

By diluting this largely with water, and adding an excess of ammonia, a brownish-red color is obtained.

NARCOTINE.

This alkaloid occurs along with morphine in opium. It is scarcely, if at all, soluble in cold water. Alcohol dissolves it slowly, chloroform very readily.

The following tests may be employed to distinguish narcotine:

1°. Strong nitric acid forms with narcotine a colorless solution, which turns yellow on heating.

2°. Chlorine water gives a yellowish-green color with solutions of narcotine salts. Ammonia added to this gives a bright yellowish-red.

3°. Sulphuric acid forms a violet, or in some cases a yellow, solution with narcotine. When heat is slowly applied an orange-red is obtained, and this changes to a bluish-violet. Further heat produces a blue, and if the solution is now cooled a deep red results.

The following is the U. S. P. process for the valuation of opium:

ASSAY OF OPIUM.

Opium, in any condition to be valued.....	7 Gm.
Lime, freshly slaked.....	3 Gm.
Chloride of ammonium.....	3 Gm.
Alcohol and stronger ether, sufficient.	
Distilled water, sufficient.	

Triturate together the opium, lime, and 20 C.c. of distilled water in a mortar, until a uniform mixture results; then add 50 C.c. of distilled water, and stir occasionally, during half an hour. Filter the mixture through a plaited filter, three to three and one-half inches (75 to 90 millimeters) in diameter, into a wide mouthed bottle or stoppered flask having the capacity of about 120 C.c. and marked at exactly 50 C.c., until the filtrate reaches this mark. To the filtered liquid (representing 5 Gm. of opium), add 5 C.c. of alcohol and 25 C.c. of stronger ether, and shake the mixture; then add the chloride of ammonium, shake well and frequently during half an hour, and set it aside for twelve hours. Counterbalance two small filters, place one within the other in a small funnel, and decant the ethereal layer as completely as practicable upon the filter. Add 10 C.c. of stronger ether to the contents of the bottle and rotate it; again decant the ethereal layer upon the filter, and afterward wash the latter with 5 C.c. of stronger ether, added slowly and in portions. Now let the filter dry in the air, and pour upon it the liquid in the bottle, in portions, in such a way as to transfer the greater portion of the crystals to the filter. Wash the bottle, and transfer the remaining crystals to the filter, with several small portions of distilled water, using not much more than 10 C.c. in all, and distributing the portions evenly upon the filter. Allow the filter to drain, and dry it, first by pressing it between sheets of bibulous paper, and afterward, at a temperature between 55° and 60° C. (131° to 140° F.). Weigh the crystals in the inner filter, counterbalancing by the outer filter. The weight of the crystals in grammes, multiplied by *twenty*, equals the percentage of morphine in the opium taken.

STRYCHNINE.

Strychnine comes to us as the pure alkaloid, $C_{21}H_{22}N_2O_2$, and combined as sulphate, nitrate, or other salt.

The alkaloid is recognized by these tests:

1°. Strychnine is intensely bitter, and almost absolutely insoluble, in water. At 15° C. about 6,700 parts are necessary for solution.

It is readily soluble in chloroform.

2°. Most of the alkaloid reagents give precipitates with solutions of strychnine salts.

Potassium sulphocyanide and mercuric chloride give fine crystalline precipitates, which, when observed under the microscope, present characteristic forms.

3°. Strychnine dissolves in strong pure sulphuric acid to a colorless fluid. If to this a small fragment of some oxidizing agent, as $K_2Cr_2O_7$ or MnO_2 , be added, and moved about with a glass rod, a deep blue violet color appears, which in time changes to wine red, and then to yellowish red.

The test is best applied in a porcelain dish, and is very characteristic.

4°. Strong nitric acid dissolves strychnine.

The solution is colorless when cold (difference from brucine), but becomes yellow on application of heat.

BRUCINE.

Brucine is found with strychnine in *nux vomica* and elsewhere.

The alkaloid is bitter and poisonous, and appears in commerce in the pure state or in several salts. The formula is $C_{23}H_{28}N_2O_4$.

The chief chemical characteristics are these:

1°. Most of the alkaloid reagents give precipitates. With tannic acid the precipitate is flocculent and dirty white, with mercuric chloride and potassium sulphocyanide, crystalline.

2°. Strong nitric acid dissolves brucine, forming a deep red liquid. This becomes yellow when heated.

Reducing agents, as stannous chloride or ammonium sulphide, added to this liquid, change its color to violet. In employing this test care must be taken to avoid using too much acid.

3°. Brucine is soluble in strong sulphuric acid, giving a light rose color. A trace of nitric acid in sulphuric acid added to this changes the color to bright red, turning yellow.

4°. Chlorine water added to brucine solutions produces a bright red color. If ammonia is afterwards added, a yellowish-brown color is obtained.

ASSAY PROCESS FOR THE DETERMINATION OF TOTAL ALKALOIDS IN SOLID EXTRACT OF NUX VOMICA.

Take 1 Gm. of the extract; dissolve it in 24 C.c. of water, heating gently if necessary, and add 6 Gm. of sodium carbonate previously dissolved in 24 C.c. of water, and then add 24 C.c. of chloroform. Shake well, warm gently, and separate the chloroform solution. Add to this 24 C.c. of diluted sulphuric acid mixed with an equal volume of water; again agitate, warm gently, and separate the acid liquid from the chloroform. To this acid liquid add now an excess of ammonia water, and agitate with 24 C.c. of chloroform. When the liquids have separated perfectly, transfer the chloroform solution to a tared capsule and evaporate to dryness on a water-bath. Heat the residue for one hour on the water-bath, and then weigh. (The weight of the dry residue in Gm. multiplied by 100 represents the per cent. by weight of total alkaloids in the extract.)

ASSAY PROCESS FOR DETERMINING THE TOTAL ALKALOIDS IN LIQUID EXTRACTS (FLUID EXTRACT, TINCTURE AND OTHER PERCOLATES) OF NUX VOMICA.

Take 24 C.c. of the liquid; evaporate almost to dryness on a water-bath; dissolve the residue in 6 C.c. of chloroform and 12 C.c. of diluted sulphuric acid with 12 C.c. of water; agitate, and warm gently. When the liquids have separated, draw off the chloroform, and add to the acid liquid an excess of ammonia water and 12 C.c. of chloroform; shake well, warm gently, and after the liquids have again separated completely, transfer this chloroform solution to a weighed dish, evaporate over a water-bath, and dry the residue for an hour at 100° C. (212° F.). Let the residue (the total alkaloids) cool, and then weigh. (The weight of crystals in Gm. multiplied by 5 represents the percentage by weight of total alkaloids contained in the liquid examined.)

URINE ANALYSIS.

CHAPTER XLV.

OUTLINE OF TESTS.

In the practical analysis of urine, such as is customary for clinical purposes, comparatively few tests are required, and little apparatus is necessary beyond that already used for other examinations.

Frequently a single test is sufficient to determine all the physician needs to know, as to the presence or absence of sugar or albumen, for instance.

In the following pages those tests and processes will be described which experience has shown to be amply sufficient for all practical requirements. They may be summarized as follows:

- 1°. Determination of specific gravity.
- 2°. Observation of color and reaction.
- 3°. Testing for albumen.
- 4°. Testing for sugar.
- 5°. Testing for coloring matters.
- 6°. Testing for biliary acids.
- 7°. Determination of uric acid.
- 8°. Determination of urea.
- 9°. Determination of phosphates.
- 10°. Determination of chlorides.
- 11°. Examination of sediment.

SPECIFIC GRAVITY.

The density or specific gravity of the urine secreted in 24 hours, varies in health between rather wide limits, probably between 1.005 and 1.030. 1.020 may be taken as about the mean value at 15° C.

The specific gravity depends on the amounts of liquid and solid food taken, and on the loss of water from the skin by perspiration. When this loss is great the specific gravity of the urine is correspondingly increased, other things being equal.

In disease the density may be lowered below or increased above the normal value.

For an absolutely exact determination of the density the use of the pycnometer, Mohr-Westphal balance, or other apparatus is necessary. But for our purpose the *urinometer*, or density bulb, is sufficiently accurate. This little instrument is shown in Fig. 25 at H. The urine to be tested is poured into a narrow jar, about one Cm. wider than the bulb, and, after the air bubbles have escaped, the urinometer is immersed in it. When it comes to rest the degree at which it stands is read off, *below the surface*. Usually, the last two figures only of the density are marked on the stem, as 25, instead of 1.025.

As the density of urine decreases about one degree for an increase in temperature of 3° C. it is important that the test be made at a definite known temperature, as 15° or 25° C.

By noting the amount of urine passed in 24 hours, and the density of the mixed liquid, a rough determination of the solid matters contained in it can be made. For this purpose it is simply necessary to multiply the last two figures of the density by 2.33 (known as the coefficient of Haeser), which gives the approximate number of Gm. in a liter. By proportion the amount for the day can be calculated from this.

For example, 1,400 C.c. of urine was passed, and its density was found to be 1.024,

$$\text{Then, } 24 \times 2.33 = 55.92.$$

$$\text{and, } 1000 : 1400 :: 55.92 : x = 78.288.$$

This calculation is frequently of service.

COLOR AND REACTION.

In health, the reaction of the mixed urine for 24 hours is always acid, and its color straw yellow. Many circumstances may produce a change in color, however. Increased consumption of water or decreased

perspiration would both tend to dilute the urine and lighten its color, while it may become darker from the action of causes tending to concentrate it.

In disease, various peculiar shades may be observed, from the admixture of abnormal coloring matters. For the significance of these the student must consult works on the pathology of the urine.

TESTING FOR ALBUMEN.

Albumen occurs pathologically in the urine, and numerous tests have been proposed for its detection.

Nearly all of these depend on the fact that the soluble serum albumen, which finds its way into the urine, can be coagulated and made visible as white flocculi, or as a white cloud when present in small quantity. Of the various methods of producing this coagulation, only those will be mentioned which are most characteristic, and practically the most useful.

1°. *Coagulation by heat.* When a sample of urine is boiled a precipitate usually forms. This in most cases consists of *earthy phosphates*, and is often sufficient to conceal a precipitation of albumen possibly present. If now to the boiled sample about one-tenth its volume of strong nitric acid be added, the precipitated phosphates will disappear, while the albumen will remain coagulated. It is necessary to add as much nitric acid as is here indicated, *because a small amount may sometimes dissolve coagulated albumen, forming soluble acid-albumen.* This acid albumen is broken up on the addition of more acid.

Even when boiling does not throw down a precipitate, the addition of nitric acid cannot be omitted, as under certain circumstances boiling may produce a soluble combination between alkalies present and albumen, which is stable. Nitric acid in sufficient quantity will break up this combination, and bring about coagulation.

If the urine is cloudy to begin with it should be filtered before applying these tests.

2°. *Coagulation by nitric acid.* As indicated above, nitric acid can coagulate albumen, and this test is frequently employed without previous boiling.

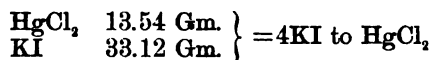
Several C.c. of the strong acid are warmed in a test-tube, and over this is carefully poured an equal volume of urine, so as to overlie without mixing. If albumen is present a white ring appears at the surface between the two liquids. When the urine contains an excess of coloring matter the ring is variously tinted.

If urine is poured over cold acid, a precipitate may appear which is not albumen. This can happen when the urine is highly charged with urea, in which case crystalline nitrate of urea will separate out, or where urates are abundantly present, in which case the ring will consist of very fine crystals of uric acid or acid urates. Both of these precipitates are dissipated by heat, and if the nitric acid is previously warmed, they cannot appear. It is better to make the test as just described than to use cold acid, and then try to warm a ring formed, as this would cause an admixture of the liquids sufficient to obscure a slight amount of albumen.

It is sometimes recommended to pour the urine in a test-tube, and then, by means of a pipette, to bring the acid under it. This modification works very well, but the acid should be warm, as before. When but a trace of albumen is present, a ring will not appear immediately, but after standing. It is well, therefore, in doubtful cases to set the tube aside for twelve hours and then observe it. If a ring is now to be seen, heat should be very carefully applied to determine whether it is albumen, or the substances just mentioned.

3°. *Tanret's "double iodide" test.* A solution of mercuric iodide in potassium iodide precipitates albumen from acidified urine.

The test solution is prepared by dissolving



in water to make one liter of solution.

The urine to be tested, a few C.c., is strongly acidified with acetic acid, and treated with the reagent, a drop at a time. If a white cloud makes its appearance, as each drop passes down through the urine, the presence of albumen is indicated.

This test is remarkably delicate, but unfortunately a few other substances give the same reaction. It precipitates many alkaloids, but the precipitates are soluble in alcohol, while the albumen precipitate is not. It precipitates uric acid, but this dissolves by heat. The albumen precipitate does not.

The above tests do not distinguish between albumen and globulin, which sometimes is present in urine. To detect globulin the urine should be diluted until the specific gravity is about 1.002 to 1.003, and then very dilute acetic acid is to be added to acid reaction. The globulin may separate out during the addition of the water, before acidifying.

Instead of adding acetic acid a current of CO_2 can be passed in for some hours. After the separation of the globulin the clear liquid can be used for albumen tests.

Fibrin may sometimes find its way into the urine and appear as a stringy mass. This should be filtered off and washed with water, and then treated with a 10 per cent. solution of sodium chloride. Fibrin dissolves in such a solution.

Other forms of albuminous matter have been occasionally detected in the urine; but their occurrence is too rare, and their detection usually too difficult, to warrant a description here.

The student will find a full discussion of this subject in Neubauer and Vogel's "Analysis of Urine."

TESTING FOR SUGAR.

Under pathological conditions several varieties of sugar have been detected in urine, but it will be necessary to describe the tests for one of these forms only, viz., grape sugar, dextrose or glucose.

Usually a urine containing sugar is characterized by a relatively high specific gravity, so that this in itself is an indication. It must be observed, however, that the statements of many of the books on this point are a little misleading.

A specific gravity of 1.030 and a volume of 1500 C.c. daily are not necessarily signs of the presence of sugar, as this density may be due to the presence of excessive amounts of urea and sodium chloride. Men who eat a great deal of meat with an abundance of salt pass urine of high density, and several cases of this sort have come under the observation of one of the authors where a density of 1.030 was the rule.

On the other hand, it must be remembered that sugar has been found in urine having a density of 1.020, and lower even.

Among the chemical tests for the presence of sugar, the following are the best:

1°. *Use of the Fehling solution.* The preparation of this reagent has been given under the volumetric tests. The mixture of the copper solution and alkaline tartrate should be freshly made and diluted with two or three volumes of water. Take of this fluid five to ten C.c., boil it in a test-tube, and gradually pour in the urine. If sugar is present a yellowish precipitate makes its appearance, which on further boiling changes to red. If the precipitate comes down on the addition of the first few drops of urine, sugar is present in considerable amount. If it appears only after an equal bulk of urine has been poured into the fluid, but a small amount is present, in all probability.

Instead of the Rochelle salt or other tartrate in the Fehling solution, various other substances have been proposed. Years ago Löwe and Kletzinsky recommended *glycerine* as a substitute, in the belief

that it would hold the copper hydrate in solution without producing a spontaneous precipitation of the suboxide. More recently *mannite* has been suggested for the same purpose, but there seems to be no good reason why either should be employed.

The Fehling solution prepared, as directed above, from pure materials, keeps unchanged for years (that is, the alkaline tartrate and sulphate in different bottles), and can even be used for quantitative tests with perfect safety.

It is especially necessary to use a thoroughly purified Rochelle salt in the preparation, but there is now no difficulty in finding this in the market.

2°. *The Trommer test.* In this, the final reaction is the same as above, and the same principles apply. If urine containing sugar is made strongly alkaline with potassium or sodium hydrate, and then mixed with a small amount of solution of copper sulphate, no precipitate of copper hydrate falls, as the sugar acts as does the tartrate of the Fehling liquid to hold it in solution.

The test is carried out by adding to a few C.c. of urine an equal volume of strong alkali solution, and then a few drops of the dilute copper sulphate solution. In presence of sugar a blue colored clear liquid is obtained, instead of a light blue precipitate. This, however, is not a sufficient test, as other substances sometimes present in urine act in the same way. If heat is now applied gently a yellowish-red precipitate falls. When urine containing sugar is treated in this way, but allowed to stand 24 hours *without* heating, a precipitate should appear.

This should be tried as a confirmatory test, as other organic matters, found in urine, are capable of reducing hot alkaline copper solutions to some extent. Uric acid and the urates have this property. If albumen is present it must be eliminated before trying this, or the preceding test, as it gives a precipitate with the copper solution.

3°. *The Bismuth tests.* If to a solution of sugar made strongly alkaline with potassium or sodium hydrate, a little subnitrate of bismuth be added, and heat applied, a characteristic black color will appear, due to the reduction of the bismuth salt to the state of lower oxide or metal.

To apply this test to urine, take a few C.c. in a test-tube, add excess of alkali, and about one-tenth Gm. of the bismuth subnitrate, and boil. In presence of sugar the black residue obtained is quite characteristic.

If the urine contains albumen the sulphur in this could produce black sulphide of bismuth in the working of this test. Albumen must therefore be removed, which can be accomplished in several ways. In this case it is best to employ Brücke's method:

Prepare a solution (Fron's reagent) by dissolving 7 Gm. of potassium iodide in 20 C.c. of water, and adding to this, after heating, 15 Gm. of bismuth subnitrate, freshly precipitated, and about 1 C.c. of strong HCl. Keep hot until all is dissolved. An orange-red solution is obtained.

This reagent precipitates albumen, but as it is rendered turbid by water the amount of acid necessary to prevent this for a given volume must be ascertained before it can be used with urine. This can be determined by adding a little of it (a few drops) to some water in a test-tube, and then dilute HCl until the precipitate just disappears. The test proper is then made by taking the same quantity of urine and adding the same amount of acid and the reagent.

Albumen and other disturbing substances precipitate, and can be filtered off. The clear filtrate should not be made turbid by HCl or the reagent. It is then made strongly alkaline with KOH or NaOH, and boiled. In presence of sugar a black precipitate is formed as before.

Uric acid does not cause a similar reduction of the bismuth salt.

4°. *Other tests.* The presence of sugar in urine can be shown by fermentation, that is, by converting it into alcohol and carbon dioxide; also by numerous other chemical reactions. In cases of doubt the action of the urine in the polariscope may be taken as decisive. The plane of polarized light is turned *slightly* to the left by normal urine, while a small amount of sugar causes it to deviate to the *right*.

5°. *The amount of sugar.* The per cent. of sugar present in urine can be determined by the Fehling solution as given under Volumetric Analysis.

Measure out 25 C.c. of the copper solution, 25 C.c. of the alkaline tartrate, making 50 C.c. of the deep blue liquid, and add an equal volume of strong potassium or sodium hydrate solution. Boil in a beaker or flask, and run in the urine, *previously diluted exactly with two to four volumes of water*, from a burette.

The first test gives approximately the volume of urine required, and several other trials should be made to determine the exact point.

The precipitated copper suboxide settles rather slowly from urine. It may be necessary to dilute the Fehling solution with water, after adding the alkali, in such cases.

In urine testing 1 C.c. of the Fehling liquid may be taken as equivalent to 5 Mg. of glucose. Extreme accuracy is not possible, as in the titration of pure water solutions.

Albumen, if present, must be coagulated by heat and a few drops of acetic acid, and filtered off.

TESTING FOR COLORING MATTERS.

Notwithstanding the numerous investigations which have been carried out on this subject, the real coloring matters of normal urine are not known with certainty.

A number of decomposition products have been described by different investigators.

a. NORMAL COLORS.

1°. *Urobilin*. This is looked upon by several authors as the chief urinary pigment. It is a reddish-brown amorphous substance, not very soluble in water, but soluble in chloroform, ether, alcohol and alkaline solutions.

In many normal urines it can be detected only with difficulty. The following methods may be employed :

Add ammonia water to strong alkaline reaction and filter, if necessary. Then add a few drops of solution of zinc chloride, but not enough to give a permanent precipitate. In this way a zinc salt is formed, which shows a peculiar greenish fluorescence.

Very few normal urines contain enough of the coloring matter to give this test. It can usually be shown by the following :

Precipitate 200 C.c. of urine with basic lead acetate. Wash the precipitate with water and dry it. Then wash it with alcohol.

Finally, digest with alcohol containing a little sulphuric acid, and filter. The filtrate is usually fluorescent. Make it strongly alkaline with ammonia and add solution of zinc chloride. This will give the fluorescence referred to above if but little is added; while if an excess of the zinc chloride is added, a reddish precipitate falls.

2°. *Urophain*. This is the name given by Heller to a substance indetical with, or simliar to, urobilin. Heller gives this test : Take a few C.c. of strong sulphuric acid in a conical glass and pour on it. drop by drop, about twice as much urine. As the two mix, a deep garnet red is produced.

This reaction is not, however, characteristic, as several other matters may give it.

3°. *Urohæmatin* is the name given by Harley to a coloring matter similar to the above. He applies this test : Dilute or concentrate the urine so that it is equivalent to 1,800 C.c. for the 24 hours. Take a few C.c. in a test-tube or wine-glass and add one-fourth of its volume of strong nitric acid. No change of color can be observed if the uro-

hæmatin is present in normal amount. If more than this is present various shades from pink to red may be produced.

4°. *Indican* is found in normal urines in very small amount only. It may, under favorable circumstances, be found as here given: Take about four C.c. of pure hydrochloric acid in a test-tube and add about half as much urine, shaking well. A blue or violet color shows indican.

A more generally applicable method is this: To 10 C.c. of urine and the same volume of strong pure HCl add 2 or 3 C.c. of chloroform. Then add, drop by drop, solution of sodium hypochlorite, shaking after each addition. The hypochlorite acts as an oxidizing agent, liberating the coloring matter, which is then taken up by the chloroform.

The oxidation must not be carried too far: that is, too much hypochlorite must not be added, as it would then destroy the color as fast as formed.

Albumen must be separated by coagulation before applying either of these tests.

b. ABNORMAL COLORS.

In disease several other coloring matters may appear in urine, the most important of which are those of the bile and blood.

1°. *Biliary colors.* Numerous tests have been given for the detection of these:

(Gmelin's test). Pour in a test-tube about 5 C.c. of urine, and by means of a small pipette bring under this about the same volume of nitric acid containing some nitrous acid. If this is carefully done, the liquids will not mix very much, and where they join several colored rings can be seen, of which the green is characteristic.

Fleischl modified this test by mixing the urine with solution of sodium nitrate, and then adding strong H_2SO_4 by a pipette so as to form a layer below. Nitric acid is liberated, and acts as above.

(Trousseau's test). Add to some urine in a test-tube several drops of tincture of iodine. If the bile pigments are present, the urine assumes an emerald green color.

2°. *Blood coloring matters.* Blood itself in urine can be best detected by means of the microscope. Sometimes its essential coloring matter can be found, when the presence of corpuscles cannot be shown.

(Heller's test). Make the urine strongly alkaline by sodium hydrate and boil in a test-tube. This precipitates the earthy phosphates, which are colored *blood red* by the separated hæmatin.

(Struve's test). Make the urine slightly alkaline by sodium hydrate solution, and add solution of tannic acid in acetic acid, sufficient to

change the reaction. If hæmoglobin is present a colored precipitate of hæmatin tannate falls.

(Almen's test). Add to about 3 C.c. of spirits of turpentine an equal volume of fresh tincture of guaiacum and shake until an emulsion forms. Add to this the urine, drop by drop. If blood-coloring matter is present, the precipitated guaiacum is colored blue, while with normal urine it is dirty white.

TESTING FOR BILIARY ACIDS.

There is no simple test which can be applied directly to the urine which will give a certain indication of the presence of these acids. They must first be separated from the large amount of other substances present, which can be done in this way (Neukomm):

Evaporate 300 to 500 C.c. of urine nearly to dryness; extract with ordinary alcohol, evaporate this solution, and extract the residue with absolute alcohol.

Evaporate this and take up the residue with water. Precipitate the solution by lead acetate, *avoiding excess*; allow to settle, wash with water on a filter, and dry by pressing between bibulous paper. This leaves an impure lead salt of the acids. Extract it with hot alcohol, and filter; add sodium carbonate to the filtrate, evaporate to dryness and extract the sodium salt, thus formed, with absolute alcohol. Evaporate again, add some water and apply the *Pettenkofer* test, as follows:

To the solution add one or two drops of a 20 per cent. cane sugar solution, and then some strong sulphuric acid, slowly, to avoid heating.

It is best to immerse the test tube in water to keep the temperature below 60° C.

As the acid mixes with the liquid, a violet or purple color is produced.

Kuelz recommends to evaporate the solution on a water-bath to dryness, to moisten the residue with a drop of dilute sugar solution, and then with a drop of the strong acid. The color appears almost immediately, but can be sharpened by heating the evaporating dish a few seconds on the water-bath.

Applying either of these tests directly to urine is unsafe, as the coloring and other matters present would interfere very much with the reaction.

TESTING FOR URIC ACID.

Uric acid occurs in the urine combined with several bases.

Allowed to stand, urine frequently deposits it as a sediment, in which it can readily be detected by means of the microscope.

Its presence may also be shown in the sediment by this test:

Throw the sediment on a filter and wash once with water. Place the residue in a porcelain dish, add a drop of strong nitric acid, and evaporate to dryness on the water-bath. A yellow or brown mass is obtained, and this touched with a drop of ammonia water turns purple (*murexid test*).

The *amount* of uric acid can be approximately determined by taking 200 C.c. of urine and adding 20 C.c. of strong hydrochloric acid. This liberates uric acid from its combinations. Allow the liquid to stand 48 hours in a cool place. Collect the sediment on a weighed filter, wash it with cold water, dry and weigh it.

The precipitate is not quite pure, but contains other substances. On the other hand uric acid is not quite insoluble, and some is dissolved by the wash-water.

When more than 30 C.c. of the latter is used it is necessary to add a correction to the weight of the acid on the filter. For every 100 C.c. of wash-water and filtrate, *Schwanert* advises to add 4.8 Mg.

In presence of albumen it is necessary to coagulate and filter.

The day's urine can contain 400 to 800 Mg.

DETERMINATION OF UREA.

Urea occurs normally in urine, being the chief nitrogenous constituent. It can readily be found by concentrating 50 C.c. of urine to half its bulk, cooling, and adding a few C.c. of strong nitric acid. The urea separates out as nitrate in glistening plates.

Its amount can be readily and accurately determined by several methods:

LIEBIG'S METHOD.

The principles upon which this method is based are these:

A dilute solution of mercuric nitrate precipitates a dilute urea solution, according to this equation:



This precipitate is white, and contains 10 parts of urea for every 72 parts of HgO. 72 Gm. of HgO dissolved in HNO₃ should precipitate, therefore, 10 Gm. of urea.

The same solution of mercury gives a yellow precipitate with solution of sodium carbonate, which is used as an *indicator*.

If the mercury solution in a burette is run into the urea solution, and from time to time a drop is removed and brought in contact with

the sodium carbonate, a point is reached where the urea is all combined, and the excess of mercury gives a yellow precipitate with the sodium carbonate. However, working in this way, for 10 parts of urea *more* than 72 parts of mercuric oxide are required, according to Liebig and Pflueger 77.2 parts.

Prepare the following solutions:

1. Solution of urea containing 2 per cent.

Dissolve 2 Gm. of pure urea, to make 100 C.c. of solution.

2. Standard mercuric nitrate solution, of which 1 C.c. will correspond to 10 Mg. of urea, or one-half C.c. of the urea solution.

Dissolve 77.2 Gm. of HgO or 71.5 Gm. of Hg in strong nitric acid. Evaporate with addition of more HNO_3 , until no more red fumes are produced, and concentrate to thickness of a syrup. Now add water gradually, and finally enough to make a liter of cold solution.

If a basic precipitate separates out, allow it to settle, dissolve it in a little HNO_3 , and add it to the solution before making up to a liter.

3. Saturated solution of sodium carbonate.

4. Baryta solution.

One volume of cold saturated solution of barium nitrate, mixed with two volumes of cold saturated solution of barium hydrate.

Measure off 10 C.c. of the urea solution in a beaker and run in about 18 C.c. of the mercuric nitrate from a burette. Shake well, and by means of a glass rod bring a drop in contact with a drop of the sodium carbonate solution on a dark glass plate. No yellow precipitate should appear yet. Continue the addition of the mercury solution until on bringing the drops in contact a yellow precipitate is just visible. If the mercury solution is correct, 20 C.c. should be required for this.

Before testing urine, phosphates and other substances interfering with the reaction must be removed. To this end 40 C.c. of urine and 20 C.c. of the baryta solution are mixed, well shaken, and filtered through a dry filter. The filtrate is alkaline if enough baryta solution has been added.

15 C.c. of the filtrate contain 10 C.c. of urine, and the solution so prepared is ready for titration, as above.

Where great accuracy is desired, several corrections must be made in the process. The chlorides in the urine combine with the mercuric

nitrate, and no precipitate of urea is formed until they have been completely converted into HgCl_2 . About 2 C.c. of the mercury solution is required for this; but to make an accurate test it is necessary to precipitate out the Cl as AgCl by a process soon to be given. The liquid, filtered through a dry filter, is ready for the baryta solution.

Another correction is necessary where the amount of urea present exceeds 3 per cent.

The mercury solution was standardized by a solution of urea containing 2 per cent., and if the urine tested contains much in excess of that, the following correction is necessary: If over 30 C.c. of the mercury solution are required for the 15 C.c. of filtrate from the baryta precipitate, half as many C.c. of water as this excess is above 30 must be added before making a second titration.

Where much below 30 C.c. is employed, for every 4 C.c. of such deficiency subtract .1 C.c. from the amount used, and make the calculation from this.

If albumen is present it should be coagulated by boiling with a drop of acetic acid, and filtered off.

Two per cent., or about 30 Gm. daily, may be taken as the mean amount of urea secreted.

BY LIBERATION OF NITROGEN.

A solution of urea is decomposed by a solution of a hypochlorite or hypobromite, according to the following equation:



By adding to the urea solution a strongly alkaline solution of the hypobromite, the liberated CO_2 would be absorbed, and the nitrogen alone would escape in the gaseous state. It is simply necessary to collect and measure this gas accurately to determine the weight of urea decomposed.

As 60 parts of urea furnish 28 parts of nitrogen, 1 Gm. will evolve 371.4 C.c., measured at 0°C . and 760 Mm. bar. From which it follows that 1 C.c. of gas corresponds to .00269 Gm. of urea.

Several forms of apparatus have been suggested for the collection of the nitrogen. The form shown in Fig. 22 is sufficiently convenient for all practical purposes.

The large jar is filled with water in which stands a burette, the larger end down.

The drawn out end is connected by means of rubber with a small wide-mouthed bottle, in which is poured the hypobromite solution, and in which is placed, also, a small test tube containing the urine to be decomposed.

By inclining the bottle the hypobromite and urine mix, when the reaction commences. The gas liberated displaces water in the burette, and can be thus measured.

Prepare the hypobromite solution as follows:

Dissolve 100 Gm. of good sodium hydrate in 250 C.c. of water. When this is cool, add, by means of a funnel tube, 25 C.c. of bromine, a little at a time.

This solution contains a sufficient excess of alkali to hold the CO_2 from the reaction. It does not keep very well.

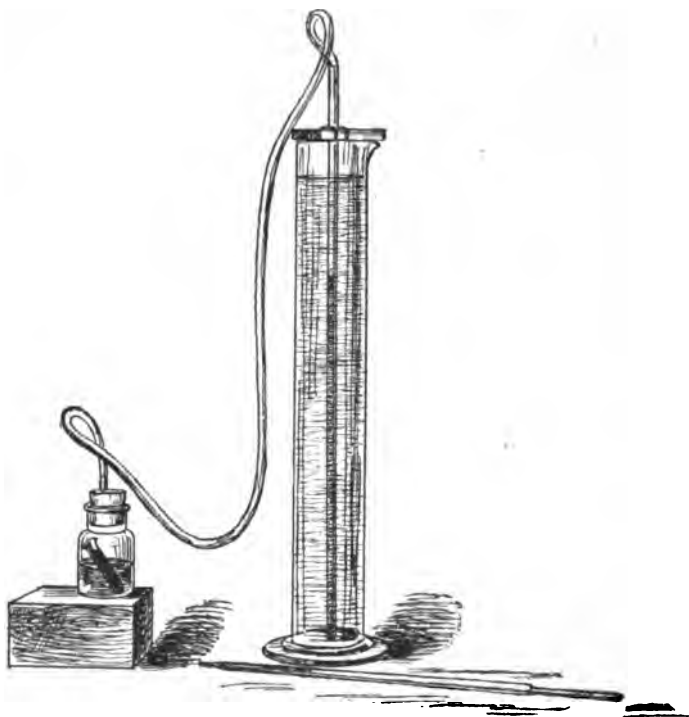


FIG. 22.

The process is carried out in this way:

Take 5 C.c. of urine in the small tube, and place this carefully in the bottle into which 15 C.c. of the hypobromite solution has already been poured. Place the burette in the jar, and when the apparatus and water have stood long enough to acquire the temperature of the air, connect it with the bottle. By means of a wooden clamp lift the burette until the water inside is on a level with that on the outside, and note the position.

Note also the temperature of the air, and the barometric height.

Now invert the bottle, and shake it from time to time. The nitrogen, or its equivalent volume of air, passes over into the burette and forces out some of the water. When, after repeatedly shaking the bottle, no increase in the volume can be observed, allow the whole apparatus to stand until the gas has become thoroughly cooled.

Then lift the burette to restore the level, and read the position again. The difference between this and the first reading is the volume of the gas at the observed temperature and pressure.

This volume can be reduced to standard conditions by the following equation:

$$V = \frac{v(B-w)}{760(1+.00366t)}$$

V = reduced volume.
 v = observed volume.
 B = barometric pressure.
 w = tension of water vapor at
 temperature t.
 t = temperature observed.

The values for w at different temperatures are given in this table (Bunsen):

10°	-----	9.165 Mm.	18°	-----	15.957 Mm.
11°	-----	9.792 Mm.	19°	-----	16.346 Mm.
12°	-----	10.457 Mm.	20°	-----	17.391 Mm.
13°	-----	11.162 Mm.	21°	-----	18.495 Mm.
14°	-----	11.908 Mm.	22°	-----	19.659 Mm.
15°	-----	12.699 Mm.	23°	-----	20.888 Mm.
16°	-----	13.536 Mm.	24°	-----	22.184 Mm.
17°	-----	14.421 Mm.	25°	-----	23.550 Mm.

Having thus the volume of the gas under normal conditions, the weight of urea corresponding can be calculated by the data already given.

The result, however, is too small, as experiment has shown that only about 92.5 per cent. of the urea present can be obtained by this method.

A correction must therefore be made.

Duggan (*Am. Chem. Jour.* IV, 47), has succeeded in obtaining the theoretical yield of nitrogen, by mixing the urine and sodium hydrate solution, and then adding the proper amount of bromine.

For practical purposes it is not necessary to make the corrections for temperature, pressure, and loss of nitrogen just referred to, as they nearly compensate each other. It will be sufficiently accurate to calculate .0027 Gm. urea for each C.c. of nitrogen.

Squibb has proposed a very simple form of apparatus with which the U. S. P. solution of sodium hypochlorite, "chlorinated soda," is used.

This places the test within reach of every practitioner, and can be heartily recommended.

Several other methods of urea determination have been described. but the above are those most generally employed.

DETERMINATION OF PHOSPHATES.

Phosphoric acid occurs in urine combined with metals of the alkaline and earthy groups. To detect the latter add ammonium or sodium hydrate solution; a bulky white precipitate falls, if the urine is normal. If coloring matters are present in abnormal amount the precipitate is not white.

The earthy phosphates seem to be held in solution very loosely: according to some authorities by carbonic acid, and according to others by ammonium chloride; so that application of heat, by driving off these substances, may cause precipitation. In testing for albumen by heat alone phosphates usually fall.

The alkaline phosphates may be detected by filtering off the earthy phosphates precipitated by ammonium hydrate, and then adding *magnesia mixture*. Under these circumstances the phosphoric acid is thrown down as white crystalline ammonium-magnesium phosphate.

The amount of phosphates present may be found by measuring off 50 C.c. of urine, adding 5 C.c. of solution of sodium acetate, heating and titrating with uranium solution as described under the head of Volumetric Analysis. The results are accurate.

About 3 Gm. daily of phosphoric acid (phosphoric anhydride, P_2O_5) may be regarded as the mean amount excreted.

DETERMINATION OF CHLORIDES.

The chlorides in urine may be detected by acidifying a small amount with nitric acid, and adding solution of silver nitrate. A white precipitate of silver chloride falls.

The amount may be determined by evaporating a measured volume (10 to 15 C.c.) to dryness in platinum, with about 2 Gm. of KNO_3 . The residue is charred to burn off organic matter, dissolved in water, and titrated with solution of silver nitrate as already explained among the volumetric tests.

According to a process recommended by Arnold, it is not necessary to evaporate the urine. Take 10 C.c. of urine, make strongly acid with pure nitric acid, then add two C.c. of solution of ferric ammonium alum, and two or three drops of solution of potassium permanganate. After shaking a few seconds the deep red color fades to light wine yellow.

The solution can now be titrated with silver nitrate and ammonium sulphocyanide, as already explained under Volumetric Analysis.

The acid and permanganate destroy coloring matters, which would interfere somewhat with the test.

The chlorides in the urine amount to ten or fifteen Gm. daily, in the mean.

EXAMINATION OF THE SEDIMENT.

On standing, urine deposits a sediment containing one or more substances, the recognition of which is frequently a matter of great importance.

The constituents of this sediment may have been in solution when the urine was passed, and settled out because of change of temperature or from other physical or chemical disturbance. Or, they may have been simply suspended in the urine, and settled out when it was brought to rest in an appropriate vessel.

The substances composing the sediment may be class as *organized* and *unorganized*, and under the latter are distinguished two groups of compounds, the *organic* and *inorganic*.

The following table gives a list of the most important bodies here recognized :

ORGANIZED.	UNORGANIZED.	
	Organic.	Inorganic.
Mucus corpuscles.	Uric acid.	Calcium carbonate.
Pus corpuscles.	Urates.	Calcium phosphate.
Blood corpuscles.	Leucin.	Calcium oxalate.
Mucin bands.	Tyrosin.	Triple phosphate.
Epithelium cells.	Cystin.	And others.
Casts of uriniferous tubules.		
Spermatozoa.		
Fungi.		

The *organized* substances are not crystalline, while most of the *unorganized* usually occur in that condition. For their recognition a microscopic examination is in most cases indispensable, and for this purpose about 100 C.c. of the urine should be allowed to stand 12 to 24 hours in a conical glass in order that the sediment may have ample time to settle out. The supernatant liquid is then poured off, and by means of a pipette a small drop of the residue is transferred to a clean slide, covered with a piece of thin glass, and placed on the stand of the microscope, ready for examination. An amplification of 250 diameters is perhaps the most convenient to employ.

For an explanation of the origin and diagnostic value of these deposits the student must consult works on the pathology of the urine.

The chief forms are shown in plates I, II, III, IV and V.

APPENDIX.

Table of Symbols and Atomic Weights used in this Book.

Element.	Symbol	Atomic weight.	Element.	Symbol	Atomic weight.
Aluminium	Al	27	Lithium	Li	7
Antimony	Sb	120	Magnesium	Mg	24
Arsenic	As	75	Manganese	Mn	53.9
Barium	Ba	137	Mercury	Hg	200
Bismuth	Bi	207.5	Molybdenum	Mo	95.5
Boron	B	11	Nickel	Ni	58
Bromine	Br	79.8	Nitrogen	N	14
Cadmium	Cd	112	Oxygen	O	16
Calcium	Ca	40	Phosphorus	P	31
Carbon	C	12	Platinum	Pt	194.8
Cerium	Ce	140.5	Potassium	K	39
Chlorine	Cl	35.4	Silicon	Si	28
Chromium	Cr	52	Silver	Ag	107.7
Cobalt	Co	59	Sodium	Na	23
Copper	Cu	63.2	Strontium	Sr	87.4
Fluorine	Fl	19	Sulphur	S	32
Gold	Au	196.2	Tin	Sn	117.7
Hydrogen	H	1	Tungsten	W	183.6
Iodine	I	126.6	Uranium	U	239.5
Iron	Fe	56	Zinc	Zn	64.9
Lead	Pb	206.5			

LIST OF REAGENTS AND TEST SOLUTIONS.

Acid, sulphuric (strong).—The commercial acid is sufficient for most purposes, where a strong acid is called for. Where the pure acid is required it will be mentioned in the text.

Acid, sulphuric (dilute).—Add one part of the above acid to four parts of distilled water, mix thoroughly, and allow to stand twenty-four hours. Then siphon, or pour off the clear liquid, which is ready for use. The strong acid must be poured into the water very slowly, and with constant stirring, to avoid a too sudden elevation of temperature.

Acid, nitric (strong).—The strong commercial acid can be employed in most cases where this acid is called for. A pure strong acid is also employed, occasionally.

Acid, nitric (dilute).—Where this acid is called for as a reagent it should be made by mixing one part of the *pure* strong acid with four parts of distilled water. It should be free from traces of chlorine and sulphates.

Acid, hydrochloric (strong).—The yellow commercial acid is largely used in the laboratory in the preparation of other substances. It is seldom pure enough to be employed as a test reagent.

A colorless acid, free from organic matter; iron and traces of sulphates must be used when the pure strong acid is called for.

Acid, hydrochloric (dilute).—This is frequently used in liberating hydrogen sulphide, carbon dioxide, and hydrogen, and for other purposes, and need not be pure. Where the dilute acid is called for as a reagent it must be made by mixing one part of the pure strong acid with four parts of distilled water.

It must be colorless, and free from traces of metals and sulphuric acid.

Acid, acetic.—Mix one part of the pure "glacial" acid with four parts of water.

Acid, sulphydric (hydrogen sulphide).—This gas is made by the action of dilute hydrochloric acid on lumps of ferrous sulphide. The gas, as liberated, is passed through a wash-bottle and then into the solution to be precipitated.

A solution of the gas in water is also frequently called for. It is made by passing the gas into water until the latter is saturated. The apparatus, Fig. 23, may be employed. The sulphide of iron is contained in the middle vessel. The acid is poured into the upper one, which is connected with the lower one by a wide tube passing through the middle one. When the escape cock is open the acid rises into the globe containing the sulphide, and produces a disengagement of the gas. Afterwards, when the cock is closed, the pressure of the gas forces the acid back into the upper globe, and thus arrests its action.

Another form is shown in Fig. 24, which explains itself.



FIG. 23.

Ammonia water.—The strong solution is seldom used in analysis. The solution usually employed is made by mixing one volume of the stronger ammonia water (containing about 28 per cent. of the gas) with three volumes of distilled water.

The solution should be free from carbonic acid, as presence of this would interfere with several of the tests where it is employed.

Ammonium carbonate.—Dissolve one part of the pure powdered crystals in five parts of dilute ammonia water.

Ammonium chloride.—Dissolve one part of the pure salt in ten parts of water.

Ammonium molybdate.—A solution of this salt is chiefly used as a test for phosphoric acid, and should be prepared in this way: Dissolve 3 Gm. of the crystals in 20 C.c. of water, and pour this solution in 20 C.c. of strong nitric acid. Warm the mixture to about 40° C. (not above), and allow to settle.

As the reagent does not keep well, it should be made only in small quantities.

Ammonium oxalate.—Dissolve one part of the pure crystals in twenty parts of water.

Ammonium sulphide.—Dilute a quantity of stronger ammonia water with an equal volume of water. Take three-fifths of this mixture and saturate it with hydrogen sulphide. Then add the remaining two-fifths of the diluted ammonia water and mix thoroughly.

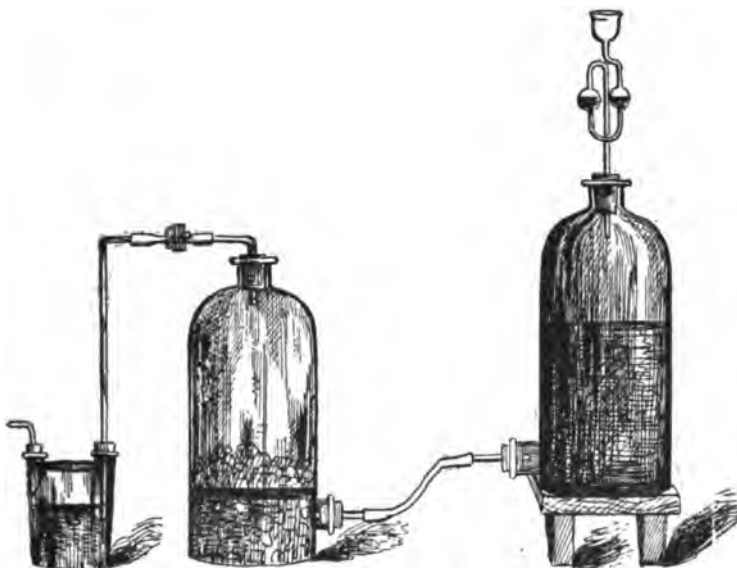


FIG. 24.

Barium chloride.—Dissolve one part of the crystals in ten parts of water.

Barium nitrate.—Dissolve one part of the crystals in fifteen parts of water.

Calcium chloride.—Dissolve one part of the fused chloride in ten parts of water, or one part of the crystals in five parts of water.

Calcium hydrate.—Slake pure white lime and pour over it a large excess of water. Allow to settle and throw away the clear liquid. Again add pure water, shake thoroughly, allow to settle as before, and decant the clear liquid into bottles for use. These bottles must be tightly stoppered. The portion rejected contains small amounts of impurities, possibly present in the lime.

Calcium sulphate.—Treat calcium sulphate, powdered, as above, and reserve the second clear solution.

Cobalt nitrate.—One part of the salt in ten parts of water.

Ferric chloride.—Dissolve one part of the yellow solid in ten parts of water. The solution should not give a blue color with potassium ferricyanide.

Ferrous sulphate.—This salt should be kept in crystals, and a little dissolved as needed.

Lead acetate.—One part of the pure crystals to ten parts of water. It may be necessary to add a few drops of acetic acid to secure a clear solution.

Litmus papers.—Red and blue, are best purchased from dealers.

Magnesia mixture.—Dissolve 100 Gm. of magnesium sulphate and 100 Gm. of ammonium chloride in 800 C.c. of water, and add 100 C.c. of strong ammonia water. Allow the mixture to stand twenty-four hours, and filter.

Mercuric chloride.—One part of the pure crystals to twenty parts of water.

Platinum chloride.—One part of the solid to twenty parts of water.

Potassium bichromate.—Dissolve one part of the pure crystals in ten parts of water. The dry powdered crystals are also used.

Potassium chromate.—Dissolve one part of the crystals, free from chlorine, in ten parts of water.

Potassium cyanide.—Keep the salt in the dry state, and dissolve when needed.

Potassium ferricyanide.—Dissolve one part of the crystals in twenty parts of water.

Potassium ferrocyanide.—Dissolve one part of the crystals in twenty parts of water.

Potassium hydrate.—Several solutions are employed in analytical chemistry. For most purposes one containing ten per cent. of the "stick" hydrate is sufficient.

Potassium iodide and starch papers.—Make a paste by dissolving one part of pure potassium iodide in 200 parts of water. Add ten parts of starch and stir until it forms an even cream. Then boil to make a smooth paste, and spread this on good unsized book-paper with a fine brush. Dry this paper, cut it in strips, and bottle for use.

Potassium nitrate.—Keep the pure salt in fine powder.

Potassium nitrite.—The salt can be obtained pure, from dealers. Keep it dry, and dissolve when needed.

Potassium sulphate.—Dissolve one part of the pure salt in 200 parts of water. This solution is used in the separation of calcium and strontium.

Potassium sulphocyanate.—Dissolve one part in twenty parts of water. Ammonium sulphocyanate is frequently used instead of this as an iron test.

Silver nitrate.—Dissolve one part in twenty parts of water.

Sodium biborate.—Keep the dry salt in powder. It is chiefly used as a flux in making beads for the cobalt, nickel and other tests.

Sodium carbonate.—Keep the pure dry salt in powder.

Make a solution of the pure crystals by dissolving one part in ten parts of water.

Sodium hydrate.—Dissolve one part of the best "stick" hydrate in ten parts of water, allow to settle, and decant the clear solution.

This solution acts on glass bottles, and soon deposits a sediment. Hence, a great deal of it should not be made at one time. The glass stoppers of bottles containing sodium hydrate, and many other substances, should be covered with a thin layer of paraffine, which prevents their sticking fast.

Sodium hypochlorite.—The "chlorinated soda" of the U. S. P. is to be used here.

Sodium phosphate.—Dissolve one part of the hydrogen-sodium phosphate in ten parts of water.

Stannous chloride.—Dissolve one part of the crystals in about twelve parts of water, adding a few drops of hydrochloric acid. Pour the clear solution in a bottle, add several small pieces of metallic tin, and close tightly. If it was necessary to add much acid to make a clear solution, the bottle must not be closed until the excess has ceased to evolve hydrogen with the tin.

OUTFIT OF APPARATUS

Sufficient to prepare small amounts of most of the preparations for which working formulæ are given in Part II:

- 1 wedgewood mortar and pestle, No. 4.
- 2 half-liter evaporating basins, of porcelain.
- 1 boiling flask, flat bottom, about 400 C.c. capacity.
- 2 glass funnels, 60 degrees angle, and about 400 C.c. capacity.
- 2 packages of white filter paper, coarse, No. 25.
- 1 half-gallon wide mouth bottle.
- 2 quart bottles, wide mouth.
- 1 four-inch horn spatula.
- 2 glass stirrers, about 20 centimeters.
- 1 sheet of red litmus paper.
- 1 sheet of blue litmus paper.
- 1 copper water-bath, 15 centimeters' diameter, without rings.
- 1 Russia-iron sand-bath dish, 12.5 centimeters' diameter.
- 1 lamp stand (Iron "retort-stand") with two rings, each ring of 10 centimeters' diameter.
- 1 ordinary Bunsen burner, single tube with adjustable valve (or a spirit lamp of 200 C.c. capacity if gas is not available).

DETERMINATION OF THE SPECIFIC GRAVITY OF LIQUIDS.

In chemical and pharmaceutical work it is frequently necessary to find the specific gravity of a liquid.

This is most accurately accomplished by means of the pycnometer, two forms of which are shown at I and J, Fig 25.

I consists of a small narrow-necked flask, with a mark on the neck. The

flask is weighed when empty and dry, and then when filled to the mark, with pure, freshly distilled water, at a definite temperature. It is then emptied, dried, filled with the liquid under examination, at the same temperature, and weighed again.

We thus compare the weights of the two liquids taken under the same conditions of volume and temperature.

The weight of the liquid, divided by the weight of the water, gives the specific gravity of the liquid.

At J another form is given. It consists of a little flask closed with a ground stopper, through which passes a capillary opening. When the flask is filled with water and closed with the stopper in such a manner that at a definite temperature the flask and capillary tube are both full, the weight of the water should be exactly 50 Gm.

The flask is filled at the definite temperature with the liquid under examination, and weighed. The weight of the liquid, divided by 50, gives the specific gravity.

G, Fig. 25, shows an ordinary *areometer*, graduated for liquids lighter than water. When immersed in pure water at a temperature of 15° C, it sinks to the point marked 1.000 on the stem. The specific gravity of lighter liquids, at the same temperature, is given by the figures (fractions) opposite the mark to which it sinks.

This instrument is very convenient, and, variously modified, is generally used. Sometimes the graduations do not indicate specific gravity, but per cent. of alcohol, sugar, soda, etc., in solutions for which they are specially constructed. The Beaumé scales are divided into equal divisions, called degrees, and are used for strong acids, alkali and other solutions.

At H, Fig. 25, is shown a urinometer, the use of which has been explained under the subject, Analysis of Urine. In construction it resembles the preceding.

A very convenient and accurate apparatus for determination of specific gravity is the Mohr-Westphal balance, shown at F, Fig. 25. From the outer end of the beam is suspended a small weight (usually in the form of a thermometer), which counterpoises the beam exactly in the air. When the weight and fine wire holding it are immersed in pure water (at 15° C.) to a definite depth, the beam is brought into equilibrium by suspending the rider A, with the weight, from the end, as shown in the figure. This indicates the specific gravity 1,000, from which it is plain that the rider is, by trial, made of the proper weight to counterbalance the upward pressure of the water.

In the figure are shown other riders, B, C, D, and E. B has the same weight as A, $C = \frac{1}{10} A$, $D = \frac{1}{100} A$, and $E = \frac{1}{1000} A$. When the sink is immersed in various liquids their specific gravities are found by keeping the rider A at the end of the beam and the other riders at different positions on the beam.

Sp. gr. 1.8456 would be indicated by A at the end of the beam, B on the division 8, C on the division 4, D on the division 5, and E on the division 6. As a rule, however, the instrument is seldom used beyond the third decimal place, but is very accurate to that limit. Where two or more of the decimal figures are the same, the lighter riders can be hung on the hooked ends of the heavier. Sp. gr. 1.444 would be represented by A on the end of the beam, B on division 4, C on a hook of B, and D on a hook of C or on the other hook of B.

The use of the balance will doubtless be understood without further explanation.

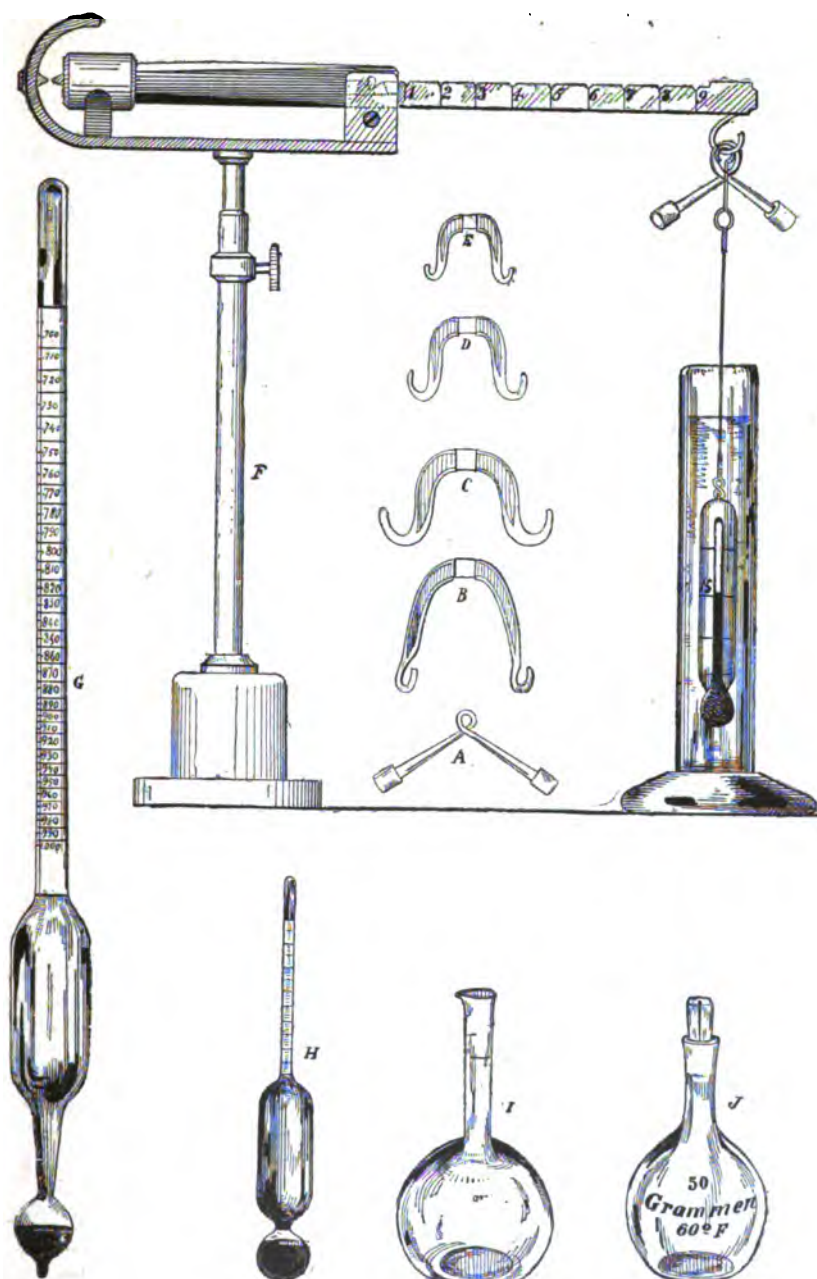


FIG. 35.

THERMOMETERS.

For measuring temperatures in ordinary chemical and pharmaceutical operations mercury thermometers are commonly employed. In this country and in England two different scales are used, the Centigrade and the Fahrenheit.

The melting point of fresh clean snow is taken as the zero point on the Centigrade scale, while on the Fahrenheit this point is marked 32°. On the Centigrade scale the boiling point of water, under a barometric pressure of 760 Mm., is taken as the second fixed temperature, and is marked 100°.

The same point on the Fahrenheit scale is marked 212°. Between the melting point of snow (or freezing point of pure water), and the boiling point of water, there are, therefore, one hundred Centigrade degrees, or one hundred and eighty Fahrenheit degrees. We have then a rule for converting the readings on one scale into equivalents of the other.

Let C represent any number of Centigrade degrees, and F any number of Fahrenheit degrees, then :

$$F = \frac{9}{5} C + 32$$

and

$$C = \frac{5}{9} (F - 32)$$

A good thermometer should satisfy these conditions: When the bulb is immersed in clean fresh snow which has been kept for some time in a room having a temperature slightly above that of freezing, and allowed to remain half an hour, it should register 0° Centigrade, or 32° Fahrenheit. In cheap thermometers a variation of one or two degrees is frequently found.

When a thermometer is suspended in the vapor of water (to which some pieces of platinum or copper have been added) boiling in a long-necked flask in such a manner that the bulb hangs about half an inch above the water, and the whole of the thread is surrounded by the steam, it should register, after remaining in the steam some time, 100° Centigrade or 212° Fahrenheit, provided the barometer is at the normal height of 760 Mm. For a decrease of 30 Mm. in the barometric height the boiling point of water is lowered 1°.1 Centigrade.

Variations of several degrees are frequently found at the boiling temperature. Supposing the instrument correct at the two fixed points, it does not follow that it is correct at intermediate points.

The graduation is made by determining the fixed points by the method indicated, and dividing the distance between them into one hundred or one hundred and eighty equal intervals. The divisions below freezing and above the boiling point are continued of the same length. If the bore of the capillary tube is perfectly uniform, these divisions or degrees must have the same value throughout. But this is never absolutely the case, and consequently there are more or less important errors in all direct thermometric readings.

It not infrequently happens in common thermometers that the errors in the neighborhood of 150° C. may amount to 10°.

The methods of determining the errors in a thermometer, after the fixed points have been correctly found, are simple enough ; but their description belongs rather to a treatise on practical physics than here.

Thermometric Equivalents.

Centigrade degrees.		Fahrenheit degrees.
260°	-----	500°
200°	-----	392°
160°	-----	320°
150°	-----	302°
140°	-----	284°
130°	-----	266°
120°	-----	248°
110°	-----	230°
105°	-----	221°
100°	-----	212°
95°	-----	203°
90°	-----	194°
85°	-----	185°
80°	-----	176°
75°	-----	167°
70°	-----	158°
65°	-----	149°
60°	-----	140°
55°	-----	131°
50°	-----	122°
45°	-----	113°
40°	-----	104°
35°	-----	95°
30°	-----	86°
25°	-----	77°
22°	-----	71°.6
20°	-----	68°
16°.66	-----	62°
15°.55	-----	60°
15°	-----	59°
14°	-----	57°.2
10°	-----	50°
5°	-----	41°
4°	-----	39°.2
0°	-----	32°
—5°	-----	23°
—10°	-----	14°
—15°	-----	5°
—17°.78	-----	0°

Common Temperatures.

	C.	F.
Freezing point of water.....	0°	+32°
Maximum density of water.....	+4°	39°.2
Standard temperature for sp. gr.....	15°	59°
Ordinary room temperature, about.....	20° to 22°	68° to 71°.6
Alcoholic fermentation active at about.....	25°	77°
"Gentle heat," U. S. P.....	32° to 38°	90° to 100°
Boiling point of stronger ether.....	37°	98°.6
Starch forms a paste with water at about.....	60°	140°
Albumen coagulates at about.....	60°	140°
Boiling point of alcohol.....	78°	172°.4
Water-bath heat, about.....	90°	194°
Boiling point of water.....	100°	212°
Oil-bath heat.....	200°	392°
Glycerin-bath heat.....	200°	392°

WEIGHTS AND MEASURES.**The Metric System.**

1 Meter = 100 Centimeters (Cm.) = 1,000 Millimeters (Mm.).

1 Liter = 1,000 Cubic-centimeters (C.c.).

1 Kilogram = 1,000 Grams (Gm.).

1 Gram = 1,000 Milligrams (Mgm.).

American Weights and Measures.

1 Yard = 3 Feet.

1 Foot = 12 Inches.

1 Gallon = 8 Pints.

1 Pint = 16 Fluidounce

1 Fluidounce = 8 Fluidrachma.

1 Fluidrachm = 60 Minims.

1 Avoirdupois pound = 16 Avoirdupois ounces.

1 Avoirdupois ounce = 437½ Grains.

1 Apothecaries' ounce = 8 Drachms.

1 Apothecaries' drachm = 60 Grains.

British Imperial Measures.

1 Imperial Gallon = 8 Pints.

1 Imperial Pint = 20 Fluidounces.

1 Imperial Fluidounce = 8 Fluidrachms.

1 Imperial Fluidrachm = 60 Minims.

Equivalents.

1 Meter	=	39.370432	Inches.
1 Liter	=	33.815	U. S. Fluidounces.
1 Liter	=	35.219	Imp. Fluidounces.
1 Cubic-centimeter	=	16.231	U. S. Minims.
1 Kilogram	=	32.151	U. S. Apoth. ounces.
1 Kilogram	=	35.274	Avoird. ounces.
1 Gram	=	15.43234874	Grains.
1 U. S. fluidounce	=	29.57	C.c.
1 Imperial fluidounce	=	28.39	C.c.
1 U. S. Apoth. ounce	=	31.1035	Gm.
1 Avoird. ounce	=	28.3495	Gm.
1 Grain	=	64.79895	Milligrams.

1 U. S. Fluidounce of Water weighs 0.95 U. S. Apoth. ounce.
 96 U. S. Fluidounces of Water weigh 100 Avoirdupois ounces.
 1 Imperial Fluidounce of Water weighs 1 Avoird. ounce.

Weight of Given Volumes of Alcohol at 22° C. (71° 6 F.).

1,000 C.c. weighs	817 Gm.
1,000 C.c. weighs	12,608 Grains.
1,000 C.c. weighs	20.267 Troy ounces.
1,000 C.c. weighs	28.819 Avoirdupois ounces.

Volume of Given Weights of Alcohol at 22° C. (71° 6 F.).

5 Gm. measures	6.12 C.c.
6 Gm. "	7.34 C.c.
7 Gm. "	8.56 C.c.
8 Gm. "	9.79 C.c.
9 Gm. "	11.01 C.c.
10 Gm. "	12.24 C.c.
12 Gm. "	14.68 C.c.
15 Gm. "	18.36 C.c.
20 Gm. "	24.48 C.c.
25 Gm. "	30.60 C.c.
30 Gm. "	36.72 C.c.
35 Gm. "	42.84 C.c.
40 Gm. "	48.96 C.c.
45 Gm. "	55.08 C.c.
50 Gm. "	61.20 C.c.
55 Gm. "	67.32 C.c.
60 Gm. "	73.44 C.c.
70 Gm. "	85.68 C.c.
80 Gm. "	97.92 C.c.
90 Gm. "	110.16 C.c.
100 Gm. "	122.40 C.c.

Weight of Given Volumes of Diluted Alcohol at 22° C. (71° 6 F.).

(U. S., 45.5 per cent., by weight.)

1,000 C.c. weighs	925 Gm.
1,000 C.c. weighs	14,374 Grains.
1,000 C.c. weighs	20.738 Troy ounces.
1,000 C.c. weighs	28.626 Avoirdupois ounces.

Volume of Given Weights of Diluted Alcohol at 22° C. (71° F.)

5 Gm. measures	-----	5.41 C.c.
6 Gm. "	-----	6.49 C.c.
7 Gm. "	-----	7.57 C.c.
8 Gm. "	-----	8.65 C.c.
9 Gm. "	-----	9.73 C.c.
10 Gm. "	-----	10.81 C.c.
12 Gm. "	-----	12.98 C.c.
15 Gm. "	-----	16.22 C.c.
20 Gm. "	-----	21.62 C.c.
25 Gm. "	-----	27.02 C.c.
30 Gm. "	-----	32.43 C.c.
35 Gm. "	-----	37.84 C.c.
40 Gm. "	-----	43.24 C.c.
45 Gm. "	-----	48.64 C.c.
50 Gm. "	-----	54.05 C.c.
55 Gm. "	-----	59.45 C.c.
60 Gm. "	-----	64.86 C.c.
70 Gm. "	-----	75.68 C.c.
80 Gm. "	-----	86.48 C.c.
90 Gm. "	-----	97.28 C.c.
100 Gm. "	-----	108.10 C.c.

Volume of Given Weights of Glycerin. Sp. Gr. 1.250.

1 Gm. measures	-----	0.80 C.c.
2 Gm. "	-----	1.60 C.c.
3 Gm. "	-----	2.40 C.c.
4 Gm. "	-----	3.20 C.c.
5 Gm. "	-----	4.00 C.c.
6 Gm. "	-----	4.80 C.c.
7 Gm. "	-----	5.60 C.c.
8 Gm. "	-----	6.40 C.c.
9 Gm. "	-----	7.20 C.c.
10 Gm. "	-----	8.00 C.c.
12 Gm. "	-----	9.60 C.c.
15 Gm. "	-----	12 C.c.
20 Gm. "	-----	16 C.c.
25 Gm. "	-----	20 C.c.
30 Gm. "	-----	24 C.c.
35 Gm. "	-----	28 C.c.
40 Gm. "	-----	32 C.c.
45 Gm. "	-----	36 C.c.
50 Gm. "	-----	40 C.c.
60 Gm. "	-----	48 C.c.
70 Gm. "	-----	56 C.c.
80 Gm. "	-----	64 C.c.
90 Gm. "	-----	72 C.c.
100 Gm. "	-----	80 C.c.

Table of Approximate Solubilities.

SUBSTANCES.	Number of C.c. of solvent required to dissolve 10 Gm. of the substance.			
	WATER.		ALCOHOL.	
	At 15° C. (59° F.)	At 100° C. (212° F.) boiling.	At 15° C. (59° F.)	At 78° C. (173° F.) boiling.
Acidum arsenosum	300—800	150	sl. sol.	sl. sol.
Acidum boricum	250	80	160	50
Acidum citricum	7.50	5	11	5
Acidum salicylicum	4500	140	25	very sol.
Acidum tannicum	60	very sol.	6	very sol.
Acidum tartaricum	7	5	25	2
Alumen	105	3	ins.	ins.
Ammonii bromidum	15	7	sl. sol.	150
Ammonii carbonas	40	decom.	decom.	decom.
Ammonii chloridum	30	13.7	1000	140
Antimonii et potassii tartras	170	80	ins.	ins.
Argenti nitras	6	1	250	40
Calcii chloridum	15	very sol.	80	14.5
Calcii hypophosphis	68	60	ins.	ins.
Cinchonidinæ sulphas	1000	40	710	120
Cinchoninæ sulphas	700	140	60	15
Cupri acetat	150	50	1800	124
Cupri sulphas	26	5	ins.	ins.
Ferri et ammonii sulphas	30	8	ins.	ins.
Ferri lactas	400	120	nearly ins.	nearly ins.
Ferri sulphas	18	3	ins.	ins.
Hydrargyri chloridum corrosivum	160	20	30	11.5
Hydrargyri cyanidum	128	30	200	60
Magnesi sulphas	8	1.5	ins.	ins.
Magnesi sulphis	200	190	ins.	ins.
Mangani sulphas	7	8	ins.	ins.
Morphinæ acetat	120	15	680	140
Morphinæ hydrochloras	240	5	680	300
Morphinæ sulphas	240	7.5	7000	1400
Plumbi acetat	18	5	80	10
Plumbi iodidum	20,000	2000	sl. sol.	sl. sol.
Plumbi nitras	20	8	ins.	ins.
Potassa	5	very sol.	20	very sol.
Potassii acetat	4	very sol.	25	20
Potassii bicarbonas	32	decom.	sl. sol.	sl. sol.
Potassii bichromas	100	10	ins.	ins.
Potassii bitartras	2100	150	nearly ins.	nearly ins.
Potassii bromidum	16	10	2000	160
Potassii carbonas	10	7	ins.	ins.
Potassii chloras	165	20	sl. sol.	sl. sol.
Potassii citras	6	very sol.	sl. sol.	sl. sol.
Potassii cyanidum	20	10	sl. sol.	sl. sol.
Potassii et sodii tartras	25	very sol.	ins.	ins.
Potassii ferrocyanidum	40	20	ins.	ins.
Potassii iodidum	8	5	180	60
Potassii nitras	40	4	ins.	ins.
Potassii permanganas	175	30	decom.	decom.
Potassii sulphas	90	40	ins.	ins.
Potassii sulphis	40	50?	sl. sol.	sl. sol.
Potassii tartras	7	5	nearly ins.	nearly ins.
Quinidinæ sulphas	1000	70	80	very sol.

Table of Approximate Solubilities.

CONTINUED.

SUBSTANCES.	Number of C.c. of solvent required to dissolve 10 Gm. of the substance.			
	WATER.		ALCOHOL.	
	At 15° C. (59° F.)	At 100° C. (212° F.) boiling.	At 15° C. (59° F.)	At 75° C. (173° F.) boiling.
Quininae bisulphas	100	very sol.	320	very sol.
Quininae hydrobromas	160	10	30	10
Quininae hydrochloras	340	10	30	very sol.
Quininae sulphas	7400	300	650	30
Quininae valerianas	1000	400	50	10
Saccharum	5	2	sl. sol.	300
Saccharum lactis	70	10	ins.	ins.
Salicinum	280	7	300	30
Santoninum	almost ins.	2500	400	30
Soda	17	8	readily sol.	very sol.
Sodii acetat	30	10	300	21
Sodii arsenas	40	very sol.	sl. sol.	600
Sodii bicarbonas	120	decom.	ins.	ins.
Sodii bisulphis	40	20	720	500
Sodii boras	160	5	ins.	ins.
Sodii bromidum	12	5	130	110
Sodii carbonas	16	2.5	ins.	ins.
Sodii chloras	11	5	400	430
Sodii chloridum	28	25	nearly ins.	nearly ins.
Sodii hypophosphis	10	1.2	300	10
Sodii hyposulphis	15	5	ins.	ins.
Sodii iodidum	6	3	18	14
Sodii nitras	13	6	ins.	sl. sol.
Sodii phosphas	60	20	ins.	ins.
Sodii pyrophosphas	120	11	ins.	ins.
Sodii salicylas	15	very sol.	60	-----
Sodii santoninas	30	5	120	24
Sodii sulphas	28	4	ins.	ins.
Sodii sulphis	40	9	sl. sol.	sl. sol.
Sodii sulphocarbolas	50	7	1300	100
Strychninae sulphas	100	20	600	20
Zinci acetat	30	15	300	30
Zinci bromidum	very sol.	very sol.	soluble	soluble
Zinci chloridum	very sol.	very sol.	soluble	soluble
Zinci iodidum	very sol.	very sol.	soluble	soluble
Zinci sulphas	6	3	ins.	ins.
Zinci sulphocarbolas	20	-----	20	-----
Zinci valerianas	1000	decom.	-----	-----

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PLATE I.

1. Crystals of "triple phosphate" or phosphate of ammonium and magnesium ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$). These are very common and are deposited from healthy urine which has become alkaline. They have also been found in urine having a decided acid reaction.
2. Crystals of triple phosphate with neutral calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), stellar form.
3. Crystals of triple phosphate from urine to which ammonia water had been added.
4. Stellar crystals of calcium phosphate, with nodules and dumbbells of the same compound. These last forms are by no means as common as the others.
5. Octahedral crystals of calcium oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$). This is a deposit very frequently met with in urine of alkaline, neutral or very slightly acid reaction.
6. Dumbbells of calcium oxalate. This modification occurs in all shapes from the true dumbbell to an almost perfect sphere, but is far less common than are the octahedra.



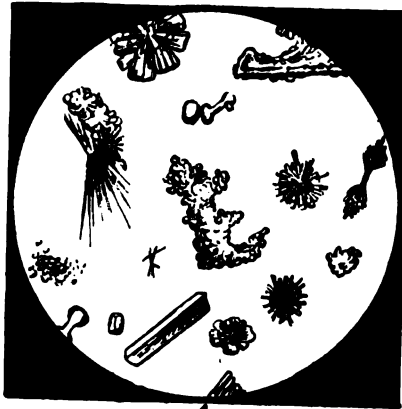
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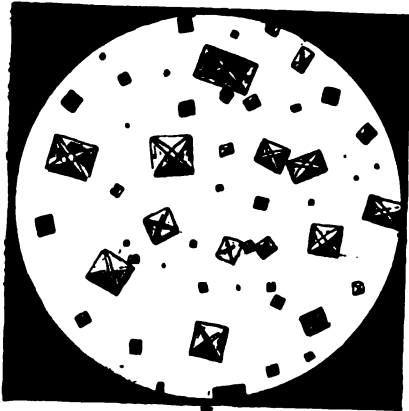
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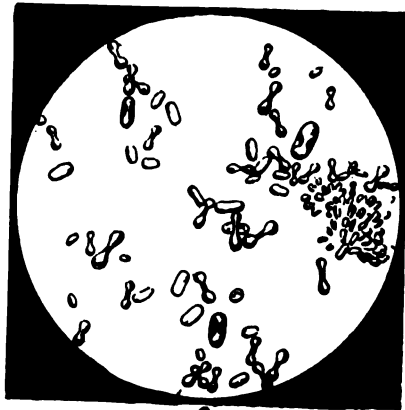
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PLATE I.



PLATE II.

1. Common forms of uric acid crystals. These have usually a yellow color or even a deep reddish yellow. Sometimes, however, they are deposited from urine almost free from color.
2. Another very common form of uric acid crystal.
3. We have here bunches of crystals which bear a slight resemblance to the stellar neutral calcium phosphate, and others which seem to consist of bundles of narrow crystalline plates.
4. Sodium urate. The smaller spiculated crystals are very common in old sediments.
5. A deposit very frequently observed, supposed to consist of ammonium urate.
6. Mixed urates of sodium and ammonium.



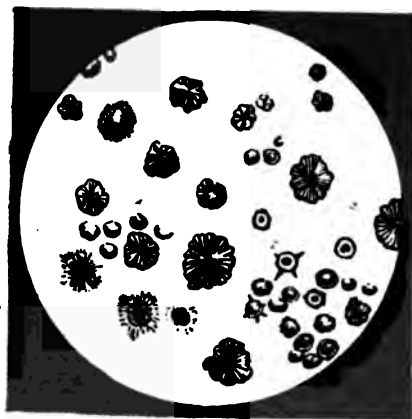
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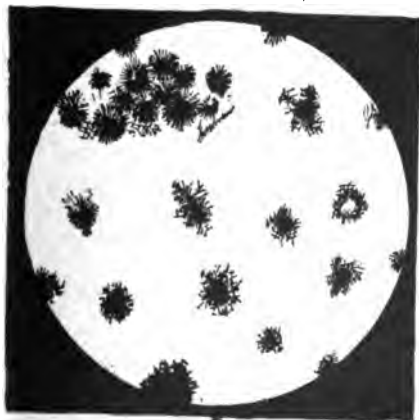
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PLATE II.

PLATE III.

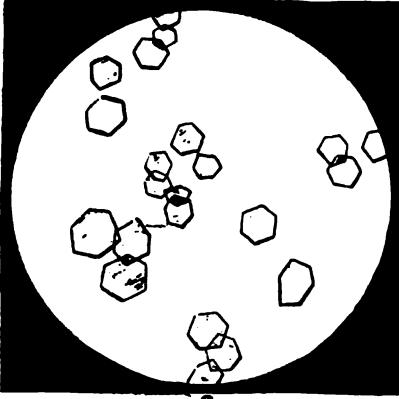
1. Spheres of leucin (amido-caproic acid,) $C_6H_{11}NO_7$. This is not a common deposit; it is found in urine in cases of acute yellow atrophy of the liver, and after acute phosphorus poisoning.
2. Needles of tyrosin, $C_9H_{11}NO_3$. Occurs sometimes with leucin and is observed in bunches of fine needles radiating from a center or in loose masses of needles crossing each other in all directions.
3. Plates of cystin, $C_2H_7NSO_2$, very thin and nearly transparent. By some authors it is regarded as a normal constituent of urine, and is frequently met with in small amount.
4. Vaginal epithelium.
5. Two forms of bladder epithelium frequently seen.
6. Commoner forms of urethral epithelium.



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PLATE III

PLATE IV.

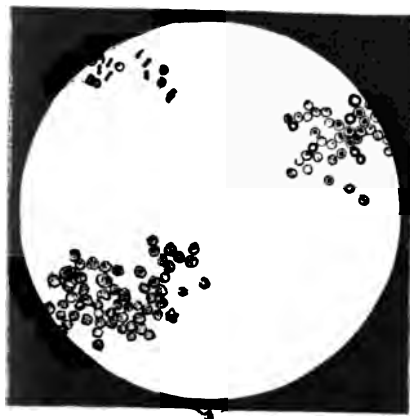
1. Blood corpuscles. Those represented in the lower part of the field have lost their sharp outlines, as is usually the case in urine which has stood for some time. Blood corpuscles, when occurring in fresh urine, are easily recognized by their yellowish color and depressed centers. Owing to this peculiar shape the center appears alternately light and dark on changing the focus of the microscope.

Sometimes the corpuscles appear as flattened disks standing on edge, as shown in the upper part of the field.

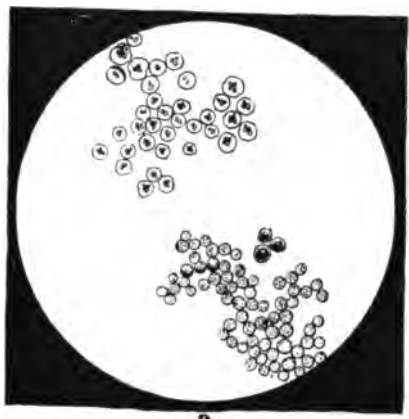
2. Pus corpuscles. The lower part of the field shows them as frequently found in urine. If when on a slide, ready for examination, a drop of dilute acetic acid is introduced under the cover glass, the nuclei are made very distinct as shown in the upper part of the field.

When urine containing pus is allowed to settle in a conical glass and the supernatant liquid then poured off the residue can be used for a characteristic test. To this end add to it some strong solution of potassium hydrate. This converts the pus into a glairy gelatinous mass which will remain in the glass when this is inverted.

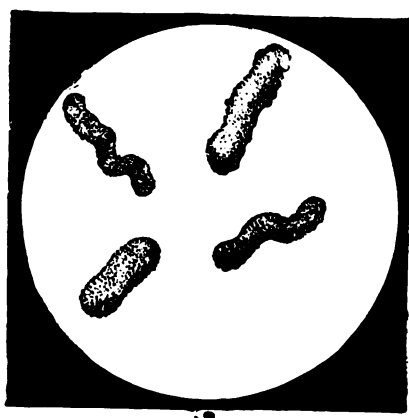
3. Well defined granular casts. These are usually recognized without difficulty.
4. Waxy casts. It is scarcely possible to give a faithful representation of the microscopic appearance of these on paper. They have, as shown, well defined outlines, but are nearly transparent and possess a peculiar waxy consistence which is easily recognized when once seen.
5. Epithelial casts, mucus corpuscles and crystals of triple phosphate, found in the same field.
6. Hyaline casts of several forms. These are usually very transparent and frequently can be found only after very patient search, with careful adjustment of the illumination; sometimes they possess considerable length and there is then danger of confounding them with stringy *mucin* bands shown in Plate V, 4.



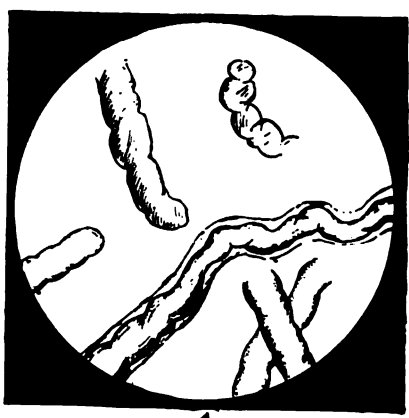
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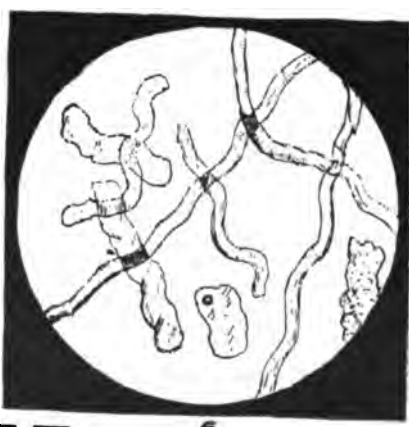
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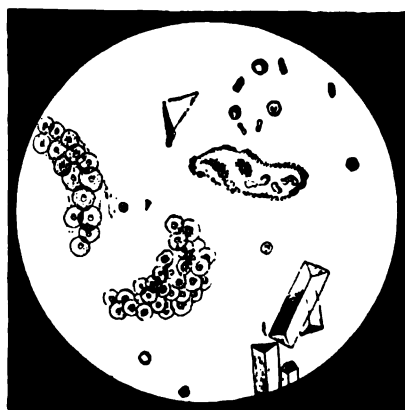
PLATE IV

PLATE V.

1. Casts showing blood corpuscles and fat globules. Both forms are easily recognized with a little practice.
Vaginal and urethral epithelium are shown in the same field.
2. Casts covered with large mucus corpuscles; another cast contains granular matter and blood corpuscles. Free blood corpuscles and crystals of triple phosphate are shown in the field.
3. Human spermatozoa.
4. Mucin bands. These are frequently of great length and have a stringy appearance; one is shown covered with a deposit of granular matter (urates). Mucin bands are found in urine free from albumen.
5. Several fungous growths found in urine. In the upper part of the field we have the jointed rods of *penicillium glaucum*; to the right the yeast fungus, *torula cerevisiae*; below, the urea ferment by which urea is decomposed giving the urine an alkaline reaction. To the left is shown a mass of yeast cells grouped around dark crystals of uric acid.
6. Foreign matters frequently found in urine.
In the upper right hand portion of the field a piece of a hair is shown; in the upper left hand a fiber from a woolen blanket: the threads in the center of the field (vertical) are cotton fibers; the three threads passing from left to right downwards are silk fibers. The student should practice on the identification of these and other matters which are likely to find their way into urine from clothing or from other source.



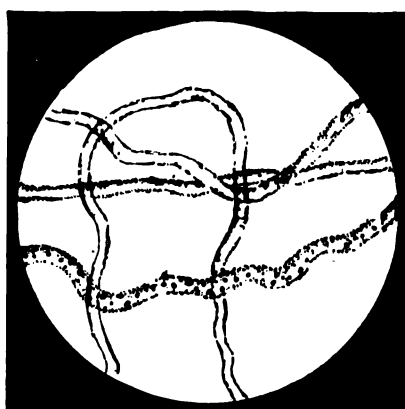
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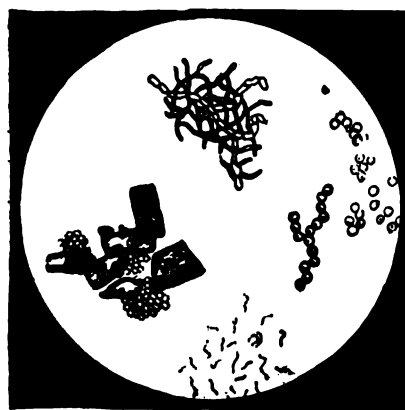
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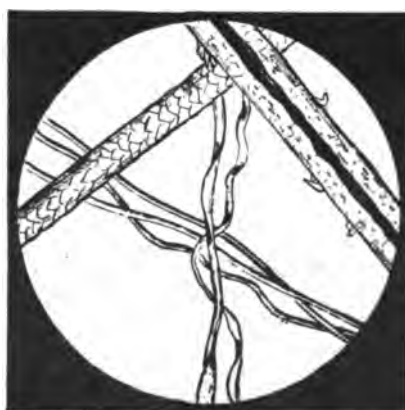
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PLATE V

